

IN THE CLAIMS

The application was originally filed with Claims 1-57. Claims 1-19, 36-49 and 51-57 were previously canceled. Claims 32, 34, 35 and 50 were previously amended. Claim 20 is currently amended. Claims 21-31 and 33 are as originally filed. New Claims 58-60 are added. Claims 20-35, 50 and 58-60 are pending. Any additions to the claims are indicated by underlining and any deletions are indicated by strikethrough. The status of the claims is shown in parenthesis at the beginning of each claim.

Claims 1 - 19 (PREVIOUSLY CANCELED).

Claim 20 (CURRENTLY AMENDED): A method of hybridizing a microarray of oligonucleotides bound to ~~an adsorbed~~ a polymer adsorbed surface on a surface of a siliceous substrate with a nucleic acid material comprising the step of incubating the nucleic acid material with the microarray of oligonucleotides on the adsorbed polymer surface in a hybridization solution at a hybridization temperature ranging from about 55°C to about 70°C so as to hybridize the nucleic acid material, wherein the hybridization solution comprises a buffer composition that comprises a pH within a range of pH 6.4 to 7.5, a non-chelating buffering agent that maintains the pH within the pH range, and a monovalent cation in a monovalent cation concentration ranging from about 0.01 M to about 2.0 M.

Claim 21 (ORIGINAL): The method of Claim 20, wherein in the step of incubating, the non chelating buffering agent is selected from a group consisting of 2-[N-morpholino]ethanesulfonic acid (MES), 3-(N-Morpholine)propanesulfonic acid (MOPS), Piperazine-N,N'-bis(2-ethansulfonic acid (PIPES), Tris(hydroxymethyl)aminomethane hydrochloride (TRIS-HCl), Hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES), and N-Tris(hydroxymethyl)methylglycine (TRICINE).

Claim 22 (ORIGINAL): The method of Claim 20, wherein in the step of incubating, the monovalent cation is selected from a salt consisting of one or more of LiCl, NaCl and KCl and the monovalent cation concentration ranges from about 0.1 M to about 2.0 M.

Claim 23 (ORIGINAL): The method of Claim 20, wherein the adsorbed polymer surface comprises a polycationic polymer.

Claim 24 (ORIGINAL): The method of Claim 23, wherein the polycationic polymer is selected from a group consisting of one or more of polyethylenediamine, poly-acrylamide, poly-L-arginine, poly-L-histidine, and poly-L-lysine.

Claim 25 (ORIGINAL): The method of Claim 20, wherein in the step of incubating, the buffer composition further comprises a chelating agent selected from a group consisting of one or more of ethylenediaminetetraacetic acid (EDTA), trans-1, 2-diaminocyclohexanetetraacetic acid (CDTA) and diethylenetriaminopentaacetic acid (DTPA) that has a chelating agent concentration of less than about 100 μ M.

Claim 26 (ORIGINAL): The method of Claim 20, wherein in the step of incubating, the buffer composition further comprises an ionic surfactant selected from a group consisting of one or more of sodium dodecyl sulfate (SDS), lithium lauryl sulfate (LLS), N-lauryl sarcoside, acylated polypeptides, linear alkybenzene sulfonates, lignin sulfonates, paraffin sulfonates, sulfosuccinate esters, alkylnaphthalene sulfonates, isethionates, alkanolamine condensates, and N-alkylpyrrolidones, and wherein the step of incubating comprises using a hybridization chamber, and the ionic surfactant is provided in an amount sufficient to wet surfaces of the hybridization chamber and loosen bubbles impinged on the surfaces of the hybridization chamber.

Claim 27 (ORIGINAL): The method of Claim 26, wherein the amount of ionic surfactant is a surfactant concentration ranging from about 0.01% to about 0.2% (w/v).

Claim 28 (ORIGINAL): The method of Claim 20, wherein the buffer composition has a total cation concentration of about 0.02 M to about 2.0 M.

Claim 29 (ORIGINAL): The method of Claim 20, wherein in the step of incubating, the non chelating buffering agent is 2-[N-morpholino]ethanesulfonic acid (MES), the monovalent cation is LiCl, the monovalent cation concentration is greater than or equal to 300 mM, the pH is within the range of pH 6.6 to 6.8.

Claim 30 (ORIGINAL): The method of Claim 29, wherein in the step of incubating, the buffer composition further comprises one or both of a chelating agent ethylenediaminetetraacetic acid EDTA having a chelating agent concentration of about 50 μ M, and an ionic surfactant selected from sodium dodecyl sulfate (SDS), lithium lauryl sulfate (LLS) having a surfactant concentration that ranges from about 0.02 % to about 0.1 % (w/v), and the buffer composition has a total cation concentration of about 750 mM.

Claim 31 (ORIGINAL): The method of Claim 20, before the step of incubating, further comprising the step of combining the nucleic acid material with the buffer composition.

Claim 32 (PREVIOUSLY AMENDED): The method of Claim 20, after the step of incubating, further comprising the step of interrogating the hybridized microarray at a first location, the first location being a physical location either where the incubation of the microarray is performed or another location separate from the microarray incubation location.

Claim 33 (ORIGINAL): The method of Claim 32, further comprising the step of transmitting data representing a result of the interrogation.

Claim 34 (PREVIOUSLY AMENDED): The method of Claim 33, further comprising the step of receiving the transmitted data at a second location, the second location being a physical location that is different from one or both of the first location where the microarray interrogation is performed and the microarray incubation location.

Claim 35 (PREVIOUSLY AMENDED): The method of Claim 34, wherein the first location is remote from the second location, the remote first location being physically separated from the second location.

Claims 36 - 49 (PREVIOUSLY CANCELED).

Claim 50 (PREVIOUSLY AMENDED): A method of performing a high temperature hybridization assay comprising the step of:

incubating a nucleic acid material with a microarray of oligonucleotides in a hybridization solution at a hybridization temperature ranging from about 55°C to about 70°C so as to hybridize the nucleic acid material,

wherein the microarray comprises a siliceous substrate with an adsorbed polymer surface and oligonucleotides bound to the adsorbed polymer surface, and

wherein the hybridization solution comprises a pH within a range of pH 6.4 and 7.5 and a buffer composition, the buffer composition comprising a non-chelating buffering agent that maintains the pH within the range and a monovalent cation having a monovalent cation concentration ranging from 0.01 M and 2.0 M.

Claims 51 - 57 (PREVIOUSLY CANCELED).

Claim 58 (NEW): A method of hybridizing a microarray of oligonucleotides with a nucleic acid material comprising the step of:

incubating the nucleic acid material with the microarray of oligonucleotides in a hybridization solution at a hybridization temperature ranging from about 55°C to about 70°C so as to hybridize the nucleic acid material, the oligonucleotides being bound to a polymer coating adsorbed on a surface of a siliceous substrate, the adsorbed polymer coating being non-covalently bound to the siliceous substrate surface,

wherein the hybridization solution comprises a buffer composition that comprises a pH within a range of pH 6.4 to 7.5, a non-chelating buffering agent that maintains the pH within the pH range, and a monovalent cation in a monovalent cation concentration ranging from about 0.01 M to about 2.0 M.

Claim 59 (NEW): The method of Claim 58, wherein the non chelating buffering agent is 2-[*N*-morpholino]ethanesulfonic acid (MES), the monovalent cation being LiCl, the monovalent cation concentration being greater than or equal to about 300 mM, the pH being within the range of about pH 6.6 to about 6.8, and wherein the adsorbed polymer coating is a polycationic polymer.

Claim 60 (NEW): A method of reducing surface degradation to a microarray of oligonucleotides during a high temperature hybridization assay comprising:

incubating a nucleic acid material with the microarray of oligonucleotides in a hybridization solution at a hybridization temperature ranging from about 55°C to about 70°C so as to hybridize the nucleic acid material, the oligonucleotides being bound to a polycationic polymer that is adsorbed to a surface of a siliceous substrate, the adsorbed polycationic polymer being non-covalently bound to the siliceous substrate surface,

wherein the hybridization solution comprises a buffer composition that comprises a pH within a range of pH 6.4 to 7.5, a non-chelating buffering agent that maintains the pH within the pH range, and a monovalent cation in a monovalent cation concentration ranging from about 0.01 M to about 2.0 M.

REMARKS

Claims 20-35 and 50 were pending and were rejected. Applicant has amended Claim 20 and has added new Claims 58-60 for consideration. Claims 20-35, 50 and 58-60 are now pending. Reconsideration and allowance of Claims 20-35, 50 and 58-60 in light of the remarks below are respectfully requested.

With respect to the pending Advisory Action, the Examiner contended that the claims do not recite the features of an adsorbed polymer surface that Applicant relies upon to distinguish over Goldberg et al., USPN 6,203,989 B1. The Examiner contended that neither the claim nor the specification defines or discloses an explanation of the term “adsorbed polymer surface”. The Examiner stated that the undersigned’s remarks can not be considered as evidence against the closest prior art in absence of a clear definition of the term “adsorbed polymer surface”.

However, MPEP 2111.01 *Plain Meaning* states “The words of a claim must be given their plain meaning unless they are defined in the specification”. Since the Examiner admitted that neither the claim nor the specification defines or discloses the explanation of the term “adsorbed polymer surface”, the terms must be given their plain meaning. It is respectfully submitted that the definition of ‘adsorption’ or ‘adsorbed’ is well known in the art and available in a variety of reference sources. Moreover, the term ‘polymer’ is well known in the art and defined in many readily available reference sources. Also, the term ‘surface’ clearly refers to a surface of the siliceous substrate and therefore needs no further definition. Exhibits A-C enclosed herewith and others cited below are references to the plain meanings of ‘adsorption’, ‘adsorbed’ and ‘polymer’, all of which support the distinguishing features of the invention over that disclosed by Goldberg et al.

Exhibit A (4 pages) – “The Condensed Chemical Dictionary”, Tenth Edition, revised by Gessner G. Hawley, Van Nostrand Reinhold Company, 1981, page 22, defines ‘adsorption’ as “Adherence of the atoms, ions or molecules of a gas or liquid to the surface of another substance, call the adsorbent (q. v.). The best known

examples are gas/solid and liquid/solid systems. ... The attractive force of adsorption is relatively small, of the order of van der Waal's forces (q. v.). ...".

At page 834, The Condensed Chemical Dictionary defines 'polymer' as "A macromolecule formed by the chemical union of 5 or more identical combining units called monomers. ..."

Exhibit B (4 pages) – "Webster's New World Dictionary", Third College Edition, Victoria Neufeldt, Editor in Chief, David B. Guralnik, Editor in Chief Emertius, Simon & Schuster, Inc., 1988, page 18, defines 'adsorb' as to collect (a gas, liquid, or dissolved substance) in condensed form on a surface" and 'adsorption' as an adsorbing or being adsorbed; adhesion of the molecules of a gas, liquid or dissolved substance to a surface."

At page 1047, "Webster's New World Dictionary" defines 'polymer' as "a naturally occurring or synthetic substance consisting of giant molecules formed from polymerization." 'Polymerization' is defined as "the process of chaining together many simple molecules to form a more complex molecule with different physical properties. ..."

Exhibit C (41 pages) - Adamson, A. W. and Gast, A. P., "Physical Chemistry of Surfaces", 6th ed., John, Wiley & Sons, Inc., New York, NY, (1997), pp. 421-459, including the numerous references provided therein. For example, for the adsorption of polymers onto a surface there are certain requirements for it to meet the accepted definition: first, the polymer must be soluble in the chosen solvent, thus it is typically limited to linear polymers, second, the polymer is usually polydisperse so that the system can act as a multicomponent system acted upon by fractionation effects, third, the adsorption is exceedingly slow compared to other diffusion limited attachments because of the large number of configurations possible at the solid-solution interface (after hours of exposure the adsorption may appear to have leveled off, but in actual fact the adsorption continues to accumulate over days or even months). Generally described by "Langmuir Equation" that describes the behavior of an adsorbate toward a surface from a dilute solution including only chemical interactions (adsorption free

energy), not covalent and is generally restricted to a single monolayer next to the surface. Very similar to the chemisorption of gases and has the same rapid decline in solid-solute interaction as one moves away from the surface.

U. S. Patent No. 5,807,522 to Brown et al (copy not included herewith) - In particular at Column 4, lines 38-42, thereof, it is stated “The substrate includes, in one aspect, a glass support, a coating of a polycationic polymer, such as polylysine, on said surface of the support, and an array of distinct polynucleotides electrostatically bound non-covalently to said coating ...”. At Column 7, lines 43-46, it is stated, “One such surface described below is a glass surface having an absorbed layer of a polycationic polymer, such as poly-l-lysine.” At Column 13, lines 58-67, it is stated “The slide is coated by placing a uniform-thickness film of a polycationic polymer, e.g., poly-l-lysine, on the surface of a slide and drying the film to form a dried coating. The amount of polycationic polymer added is sufficient to form at least a monolayer of polymers on the glass surface. The polymer film is bound to surface via electrostatic binding between negative silyl-OH groups on the surface and charged amine groups in the polymers ...”. At Column 14, lines 3-8, Brown et al. states, “According to an important feature of the substrate, the deposited polynucleotides remain bound to the coated slide surface non-covalently when an aqueous DNA sample is applied to the substrate under conditions which allow hybridization ...”.

Moreover, Curriculumvisions.com at the following website address defines ‘adsorption’ as “The process by which a surface adsorbs a substance. The substances involved are not chemically combined and can be separated. Example: the adsorption properties of activated charcoal.”

<http://www.curriculumvisions.com/Elements/ElementsGlossary.html>

The IUPAC Compendium of Chemical Terminology, 2nd Edition, 1997 at the website address provided below defines ‘adsorption’ as “An increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface

of a condensed and a gaseous phase. O.B. 85; 1990, 62, 2171”

<http://www.chemsoc.org/chembytes/goldbook/A00155.pdf>

The IUPAC Compendium of Chemical Terminology, 2nd Edition, 1997 at the website address provided below defines ‘polymer’ as “A substance composed of macromolecules. 1996, 68, 2289.”

<http://www.chemsoc.org/chembytes/goldbook/P04735.pdf>

Also the following website allows a user to search terms in the IUPAC Compendium of Chemical Terminology, such that definitions for other terms, such as those for ‘van der Waals adsorption’ or ‘physical adsorption (physisorption)’ and ‘macromolecules’, for example, may be retrieved.

<http://www.chemsoc.org/cgi-shell/empower.exe>

In light of plain definitions cited above, it is respectfully submitted that those skilled in the art know what is meant by an ‘adsorbed polymer’. In particular, one skilled in the art would know that an adsorbed polymer is a polymer adhered to a surface non-covalently using non-chemical binding, such as by surface forces, van der Waals forces, and/or electrostatic forces, for example. Therefore, it is respectfully submitted that no claim amendments are necessary to Claims 20-22, 25, 28, 31 and 50 to overcome Goldberg et al., USPN 6,203,989 B1, under 35 USC 102(a).

However, Applicant has amended Claim 20 to recite “a polymer adsorbed on a surface of a siliceous substrate” instead of “adsorbed polymer surface”. Applicant submits that this amendment is fully supported by the specification as originally filed, is not made for any reason related to the patentability of the invention in Claim 20, and more importantly, this amendment does not change or narrow the intended scope of any element of Claim 20 or the claims dependent therefrom, relative to that originally filed.

Moreover, Applicant has added new Claims 58-60 for the Examiner’s consideration. New Claim 58 is an independent claim essentially similar to Claim 20, but further includes that the oligonucleotides are bound to a polymer coating adsorbed on a surface of a siliceous substrate, and that the adsorbed polymer is non-covalently

bound to the siliceous substrate surface. Support for this new claim is provided in Applicant's specification at page 13, lines 1-5, for example, and further by the plain definitions of 'adsorption' with respect to 'adsorbed polymer', as provided above. New Claim 59 is dependent from new Claim 58 and is essentially similar to Claim 29, but further includes that the adsorbed polymer coating is a polycationic polymer. Support for new Claim 59 is found in Applicant's specification at page 14, lines 9-10, and Claims 23 and 29, as originally filed. New Claim 60 is an independent claim directed to a method of reducing surface degradation to a microarray of oligonucleotides during a high temperature hybridization assay. Support for new Claim 60 can be found in Applicant's specification at least at page 4, line 1 to page 5, line 2, page 6, lines 13-17, and page 15, lines 3-6, for example. The method includes incubating, as in Claim 20, but further includes that the oligonucleotides are bound to a polycationic polymer that is adsorbed on a surface of a siliceous substrate, and that the adsorbed polycationic polymer is non-covalently bound to the siliceous substrate surface. Additional support for new Claim 60 is also found in the support provided above for new Claims 58-59.

In order to maintain an anticipation rejection, the cited reference must disclose each and every limitation of the claimed invention in order to maintain an anticipation rejection. *In re Paulsen*, 30 F.3d 1475, 1478, 31 USPQ2d 1671, 1673 (Fed. Cir. 1994). Moreover, it is not enough that the prior art reference discloses all the claimed elements in isolation. Rather, as stated by the Federal Circuit, anticipation requires the presence in a single prior art reference disclosure of each and every element of the claimed invention as arranged in the claim. *Lindemann Maschinenfabrik GmbH v. American Hoist & Derrick Co.*, 730 F.2d 1452, 221 USPQ 481 (Fed. Cir. 1984). In addition, the allegedly anticipating reference must be enabling and describe the claimed invention sufficiently to have placed it in possession of a person of ordinary skill in the art. *In re Paulsen, supra*, at 1673. The anticipation determination is viewed from one of ordinary skill in the art. There must be no difference between the claimed invention and the reference disclosure as viewed by a person of ordinary skill

in the field of the invention. *Scripps Clinic & Research Found. v. Genentech Inc.*, 927 F.2d 1565, 18 USPQ2d 1001 (Fed. Cir. 1991).

Goldberg et al. fail to teach a method of high temperature hybridization using a microarray of oligonucleotides bound to a polymer adsorbed on a surface of a siliceous substrate or ‘adsorbed polymer surface’, as claimed in Applicant’s Claims 20-22, 25, 28, 31, 50 and new Claims 58-60. The teachings of Goldberg et al. fail to include a polymer adsorbed on a siliceous substrate surface, as presently claimed. Therefore, Goldberg et al. fail to disclose each and every feature of the present invention claimed in Applicant’s Claims 20-22, 25, 28, 31, 50 and new Claims 58-60 (*In re Paulsen*, cited *supra*), such that there does exist a clear difference between the claimed invention and the reference disclosure as viewed by a person of ordinary skill in the field of the invention (*Scripps Clinic & Research Found. v. Genentech Inc.*, *supra*). Contrary to that contended by the Examiner, one of ordinary skill would not consider the glass substrate of Goldberg as a polymer adsorbed on a surface of a siliceous substrate in light of the plain definition of ‘adsorption’. Moreover in light of the plain definition of ‘adsorption’, one of ordinary skill would not consider the Goldberg et al. disclosure of polystyrene, polytetrafluoroethylene, silicon or glass in Col. 3, lines 34-39, broadly as “adsorbed polymer surface on a siliceous substrate”, contrary to that contended by the Examiner. One skilled in the art would not know from the teachings of Goldberg et al. that any polymer disclosed by Goldberg et al. is or was adsorbed on a surface of a siliceous substrate. Therefore, Goldberg et al. fail to anticipate, or even make obvious, Applicant’s Claims 20-22, 25, 28, 31, 50 and 58-60. Reconsideration is respectfully requested.

With respect to the rejection of Claims 23, 24 and 32-35 under 35 USC 103(a) over Goldberg et al. (USPN 6,203,989 B1) in view of Reynolds et al. (USPN 6,316,608 B1), Claims 23, 24 and 32-35 are ultimately dependent from Applicant’s Claim 20 and include all of the limitations recited in Claim 20. Contrary to that contended by the Examiner, Goldberg et al. in fact fail to disclose the present invention, as claimed in Applicant’s Claim 20. Therefore, Applicant’s Claim 20 is allowable over Goldberg et al. If an independent claim is allowable over a reference,

then any claim depending therefrom is allowable. *In re Fine*, 837, F.2d, 1071, 5 USPQ 2d, 1596 (Fed. Cir. 1988). Therefore, Claims 23, 24 and 32-35 are allowable over the teachings of Goldberg et al. in view of Reynolds et al. for at least the same reasons set forth above for the allowability of Applicant's Claim 20 over the teachings of Goldberg et al.

With respect to the rejection of Claims 26-27 under 35 USC 103(a) over Goldberg et al. (USPN 6,203,989 B1) in view of Cohen, USPN 6,322,989 B1, Claims 26-27 are ultimately dependent from Applicant's Claim 20 and include all of the limitations recited in Claim 20. Applicant's Claim 20 is submitted to be allowable over Goldberg et al. Therefore, Claims 26-27 are allowable over the teachings of Goldberg et al. in view of Cohen et al. for at least the same reasons set forth above for the allowability of Applicant's Claim 20 over the teachings of Goldberg et al. *In re Fine*, cited *supra*.

With respect to the rejection of Claims 29-30 under 35 USC 103(a) over Goldberg et al. (USPN 6,203,989 B1) in view of Cohen (USPN 6,322,989 B1) and further in view of McDonough et al. (USPN 6,252,059 B1), Claims 29-30 are ultimately dependent from Applicant's Claim 20 and include all of the limitations recited in Claim 20. Therefore, Claims 29-30 are allowable over the teachings of Goldberg et al. in view of Cohen et al. and further in view of McDonough et al. for at least the same reasons set forth above for the allowability of Applicant's Claim 20 over the teachings of Goldberg et al. *In re Fine*, cited *supra*.

In light of the remarks above, reconsideration and allowance of Claims 20-35 and 50 are respectfully requested. Moreover, allowance of new Claims 58-60 is respectfully requested.

In summary, Claims 20-35 and 50 were pending and were rejected. Applicant has amended Claim 20 and has added new Claims 58-60. It is submitted that Claims 20-35, 50 and 58-60 are in condition for allowance. It is respectfully requested that Claims 20-35, 50 and 58-60 be allowed, and that the application be passed to issue at an early date.

Moreover, the Examiner is reminded to provide documentary evidence to support the Examiner's contention that the substrate materials disclosed by Goldberg et al. have an inherent characteristic of adsorption on each other should the Examiner decide not to allow Claims 20-35, 50 and 58-60 at this time. Such documentary evidence was requested in Applicant's Official Response dated May 9, 2003. It is respectfully submitted that it would be inappropriate for the Examiner to make a first office action in this RCE application final based on inherent characteristics and ignore Applicant's request for such documentary evidence. See MPEP §2144.03.

Should the Examiner have any questions regarding the above, please contact Gordon M. Stewart, Attorney for Applicant, Registration No. 30,528 at Agilent Technologies, Inc., telephone number (650) 485-2386. If the Examiner's attempt to reach the undersigned is unsuccessful, the Examiner is requested to contact the undersigned at the telephone number listed below.

Respectfully submitted,

NELSON R. HOLCOMB ET AL.

By: Elizabeth E. Leitereg
Elizabeth E. Leitereg
Attorney for Applicant(s)
Registration No. 34,101
(775) 849-3085

Exhibits A-C follow after this page.

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to Mail Stop RCE, Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450 on the date shown below.

Elizabeth E. Leitereg July 11, 2003
Elizabeth E. Leitereg Date

* * * * *

EXHIBIT A

The
Condensed Chemical
Dictionary

TENTH EDITION

Revised by

GESSNER G. HAWLEY



VAN NOSTRAND REINHOLD COMPANY

Copyright © 1981 by Van Nostrand Reinhold Company Inc.

Library of Congress Catalog Card Number: 80-29636
ISBN: 0-442-23244-6

All rights reserved. Certain portions of this work copyright © 1930, 1920, 1919 by The Chemical Catalog Co., Inc. and 1977, 1971, 1966, 1956, 1950 by Van Nostrand Reinhold Company Inc. No part of this work covered by the copyright hereon may be reproduced or used in any form or by any means—graphic, electronic, or mechanical, including photocopying, recording, taping, or information storage and retrieval systems—without permission of the publisher.

Manufactured in the United States of America

Published by Van Nostrand Reinhold Company Inc.
135 West 50th Street
New York, New York 10020

Van Nostrand Reinhold Company Limited
Molly Millars Lane
Wokingham, Berkshire RG11 2PY, England

Van Nostrand Reinhold
480 Latrobe Street
Melbourne, Victoria 3000, Australia

Macmillan of Canada
Division of Gage Publishing Limited
164 Commander Boulevard
Agincourt, Ontario M1S 3C7, Canada

15 14 13 12 11 10 9 8 7 6 5

Library of Congress Cataloging in Publication Data

Main entry under title:

The Condensed chemical dictionary.

1. Chemistry—Dictionaries. I. Hawley, Gessner
Goodrich, 1905—
QD5.C5 1981 540'.3'21 80-29636
ISBN 0-442-23244-6

further) and converted into products by casting and other techniques. See also polyurethane rubber.

adjuvant. A subsidiary ingredient or additive in a mixture (medicine, flavoring, perfume, etc.) which contributes to the effectiveness of the primary ingredient.

"Admerol."²²¹ Trademark for a long oil, oxidizing copolymer for zinc- and lead-free stains and blister-resistant paints; binder for aluminum paints and varnish oils.

"Admex."²²¹ Trademark for a series of plasticizers consisting variously of epoxidized soybean oil, tallate esters, monomeric esters and polyesters. Used in vinyl plastics.

admiralty metal. A nonferrous alloy containing 70-73% copper, 0.75-1.20% tin, remainder zinc. It offers good resistance to dilute acids and alkalies, sea water, and moist sulfurous atmospheres. Sp. gr. (20°C) 8.53; liquidus temperature 935°C; solidus temperature 900°C.

Uses: Condenser, evaporator, and heat exchanger tubes, plates, and ferrules.

"Adofoam."⁵⁴⁴ Trademark for oil-field additive used specifically in air-drilling and hydraulic fracturing to produce stable foam in fresh water, salt water, acid/water solutions, sulfur/water, and oil/water mixtures.

"Adogen."²²¹ Trademark for a series of fatty nitrogen chemicals including amines, amides, amine acetates and quaternary ammonium compounds. Available in various grades for specific applications in fabric softeners, ore separation, detergents, petroleum additives, corrosion inhibitors, bactericides, printing inks, antiblock and slip agents, water-proofing formulations and chemical intermediates.

"Adol."²²¹ Trademark for a series of industrial fatty alcohols, specifically cetyl, stearyl, and oleyl, available in a variety of grades for specific applications.

"Adomall."⁵⁴⁴ Trademark for multi-value water-fracturing additive for oil-field operations; kills bacteria, inhibits corrosion, lowers surface tension, reduces permeability damage, removes drilling mud from bore and fracture areas, and produces stable foam to return fracturing water from wells.

"Adomite."⁵⁴⁴ Trademark for oil-field additives to reduce fluid loss during hydraulic fracturing. "Adomite Mark II" functions in oil-based fracturing fluids; "Adomite Aqua" in water-based fracture fluids.

"Adoquat."⁵⁴⁴ Trademark for a quaternary ammonium salt used in waterflooding operations for secondary recovery of petroleum. It increases efficiency by inhibiting bacterial growth and reducing microbial plugging.

ADP. Abbreviation for (1) adenosine diphosphate

(q.v.); (2) ammonium dihydrogen phosphate. See ammonium phosphate, monobasic.

"Adrenalin."³³⁰ Trademark for epinephrine (q.v.).

adrenaline (epinephrine). A hormone having a benzenoid structure with the formula $C_9H_{13}O_3N$. It is obtained by extraction from the adrenal glands of cattle, and is also made synthetically. Its effect on body metabolism is pronounced, causing an increase in blood pressure and rate of heart beat. Under normal conditions its rate of release into the system is constant, but emotional stresses such as fear or anger rapidly increase the output and result in temporarily heightened metabolic activity.

Hazard: Toxic by ingestion and injection.

adrenocorticotrophic hormone. See ACTH; corticoid hormone.

adriamycin (doxorubicin). An antibiotic drug reported to be effective against such types of cancer as leukemia and cancers of the breast and bladder. It is made by fermentation of a soil fungus. Approved by FDA for clinical research, but is said to have deleterious side effects. Synthetic routes to adriamycin and its analogs have been developed.

adsorbent. A substance which has the ability to condense or hold molecules of other substances on its surface. Activated carbon, activated alumina, and silica gel are examples.

"Adsorbosil."⁴²⁵ Trademark for adsorbents for use in chromatography. "Adsorbosil"-1 is a mixture of specially purified silica gel and 10% calcium sulfate designed as a thin-layer chromatography powder; "Adsorbosil" CAB is designed for column chromatography.

adsorption. Adherence of the atoms, ions or molecules of a gas or liquid to the surface of another substance, called the adsorbent (q.v.) The best-known examples are gas/solid and liquid/solid systems. Finely divided or microporous materials presenting a large area of active surface are strong adsorbents, and are used for removing colors, odors, and water vapor (activated carbon, activated alumina, silica gel). The attractive force of adsorption is relatively small, of the order of van der Waal's forces (q.v.). When molecules of two or more substances are present, those of one substance may be adsorbed more readily than those of the others. This is called preferential adsorption.

See also absorption, chemisorption.

adsorption indicator. A substance used in analytical chemistry to detect the presence of a slight excess of another substance or ion in solution as the result of a color produced by adsorption of the indicator on a precipitate present in the solution. Thus a precipitate of silver chloride will turn red in a solution containing even a minute excess of silver ion (silver nitrate solution), if fluorescein is present. In this example, fluorescein is the adsorption indicator.

This group also includes resins for use with diisocyanate to form rigid or flexible polyurethane foams.

"Polymeg."²²⁴ Trademark for polytetramethylene ether glycols. Available in three molecular weight ranges: 1000, 2000 and 3000.

Properties: Waxy solids which melt to clear, viscous liquids at about 37° C. On supercooling (or nucleation) the liquid resolidifies. Sp. gr. 0.985 (1000 MW) to 0.982 (3000 MW) at 35° C; soluble in aromatic and chlorinated hydrocarbons; slightly soluble in water, solubility decreasing with increasing molecular weight.

Use: Polyurethane technology.

polymer. A macromolecule formed by the chemical union of 5 or more identical combining units called monomers. In most cases the number of monomers is quite large (3500 for pure cellulose), and often is not precisely known. In synthetic polymers this number can be controlled to a predetermined extent, e.g., by shortstopping agents. (Combinations of 2, 3, or 4 monomers are called, respectively, dimers, trimers, and tetramers, and are known collectively as oligomers). A partial list of polymers by type is as follows:

- I. Inorganic
siloxane; sulfur chains; black phosphorus; boron-nitrogen; silicones.
- II. Organic
 1. Natural
 - (a) Polysaccharides
starch; cellulose; pectin; seaweed gums (agar, etc.); vegetable gums (arabic, etc.)
 - (b) Polypeptides (proteins)
casein; albumin; globulin; keratin; insulin; DNA
 - (c) Hydrocarbons
rubber and gutta percha (polyisoprene).
 2. Synthetic
 - (a) Thermoplastic
elastomers (unvulcanized); nylon; polyvinyl chloride; polyethylene (linear); polystyrene; polypropylene; fluorocarbon resins; polyurethane; acrylate resins.
 - (b) Thermosetting
elastomers (vulcanized); polyethylene (crosslinked); phenolics; alkyds; polyesters
 3. Semisynthetic
cellulosics (rayon, methylcellulose, cellulose acetate); modified starches (starch acetate, etc.)

See also following entries.

polymer, addition. See addition polymer.

polymer, atactic. See atactic.

polymer, block. See block polymer.

polymer, condensation. A polymer formed by a condensation reaction (q.v.).

polymer, electroconductive. A polymer or elastomer made electrically conductive by incorporation of a substantial percentage of a suitable metal powder (e.g., aluminum) or acetylene carbon black; the proportion used must be high enough to permit the particles to be in contact with one another in the mixture. Polyelectrolytes such as ion-exchange resins, salts of polyacrylic acid and sulfonated polystyrene are electroconductive in the presence of water. Pyrolysis of polyacrylonitrile makes it electrically conductive without impairment of its structure.

polymer, graft. See graft polymer.

polymer, high. An organic macromolecule composed of a large number of monomers. The molecular weight may range from about 5000 into the million (for some polypeptides). Natural high polymers are exemplified by cellulose ($C_6H_{10}O_n$) and rubber (C_5H_8)_n. Proteins are natural high polymer combinations of amino acid monomers. The dividing line between low and high polymers is considered to be in the neighborhood of 5000 to 6000 molecular weight.

Synthetic high polymers (or "synthetic resins") include a wide variety of materials having properties ranging from hard and brittle to soft and elastic. Addition of such modifying agents as fillers, colorants, etc., yields an almost infinite number of products collectively called plastics (q.v.). High polymers are the primary constituents of synthetic fibers, coating materials (paints and varnishes), adhesives, sealants, etc. Polymers having special elastic properties are called rubbers, or elastomers (q.v.).

Synthetic polymers in general can be classified: (1) by thermal behavior, i.e., thermoplastic and thermosetting (q.v.); (2) by chemical nature, i.e., amino, alkyd, acrylic, vinyl, phenolic, cellulosic, epoxy, urethane, siloxane, etc., and (3) by molecular structure, i.e., atactic, stereospecific, linear, cross-linked, block, graft, ladder, etc. (see specific entries). Copolymers (q.v.) are products made by combining two or more polymers in one reaction (styrene-butadiene). See also cross-linking.

polymer, inorganic. A polymer in which the main chain contains no carbon atoms and in which behavior similar to that of an organic polymer can be developed, i.e., covalent bonding and cross-linking, as in silicone polymers. Here the element silicon replaces carbon in the straight chain; substituent groups are often present, forming highly useful polymers. Other inorganic high polymers are black phosphorus, boron and sulfur, all of which can form polymeric structures under special conditions. At present these have little or no commercial significance.

Note: Some authorities consider silicone resins to be semi-organic, since their substituent groups are comprised of methyl groups.

polymer, isotactic. A type of polymer structure in which groups of atoms which are not part of the

EXHIBIT B

THIRD COLLEGE EDITION

Webster's New World Dictionary

OF AMERICAN ENGLISH

VICTORIA NEUFELDT

Editor in Chief

DAVID B. GURALNIK

Editor in Chief Emeritus



Webster's New World
New York

Webster's New World Dictionary

College Edition

early 80 million desk bookshelves worldwide boast a member of the distinguished family Webster's New World Dictionaries. From *The New York Times*, most of which have adopted the College Edition as their standard first dictionary. So have the Associated Press International Press International. They know that when you need Webster's New World Dictionary.

is much more than a readable, and accurate dictionary you can find. Ever since the Webster's New World Dictionary was published 15 years ago, the Webster's New World Dictionary has been defining the English language as it is, but also as these pages you will find in-depth etymologies for American dictionary current vocabulary back to their sources. Definitions modified historical or

Dedicated
to David B. Guralnik
lexicographical mentor
and friend

Webster's New World Dictionary, Third College Edition

Copyright © 1988 by Simon & Schuster, Inc.

This edition is a major revision of Webster's New World Dictionary, Second College Edition, copyright © 1986 and 1970, 1972, 1974, 1976, 1978, 1979, 1980, 1982, and 1984 by Simon & Schuster, Inc.

All rights reserved
including the right of reproduction
in whole or in part in any form

Published by Webster's New World Dictionaries
A Division of Simon & Schuster, Inc.
Gulf + Western Building
One Gulf + Western Plaza
New York, New York 10023

WEBSTER'S NEW WORLD and colophons are registered trademarks of Simon & Schuster, Inc.

Dictionary Editorial Offices: New World Dictionaries,
850 Euclid Avenue, Cleveland, Ohio 44114

DISTRIBUTED BY PRENTICE HALL TRADE

Database design and creation by Lexi-Comp, Inc., Hudson, Ohio.

The typefaces used are Century Schoolbook and Helvetica.

Manufactured in the United States of America

2 3 4 5 6 7 8 9

Library of Congress Cataloging-in-Publication Data

Webster's New World dictionary of American English / Victoria E. Neufeldt, editor-in-chief. — 3rd college ed.

1. English language—Dictionaries. 2. Americanisms—Dictionaries.

I. Neufeldt, Victoria E.

PE1628.W5633 1988

88-1712

ISBN 0-13-947169-3 (thumb-indexed)

0-13-949280-1 (plain-edged)

0-13-949314-X (leatherkraft)

admittedly / adulthood

18

to effective voltage in a circuit carrying an alternating current; the reciprocal of impedance

ad-mit-ted-ly (ad mit'id lē, əd-) *adv.* by admission or general agreement; confessedly [*I am admittedly afraid*]

ad-mix (ad miks') *vt., vi.* [*back-form*, by analogy with MIX < *admixt*, mixed with < L *admixtus*; see fol.] to mix (a thing) in; mix with something

ad-mix-ture (ad miks'char) *n.* [*< L admixtus*, pp. of *admiscere* < *ad-*, to + *miscere*, to MIX + *-ure*] 1 a mixture 2 a thing or ingredient added in mixing

ad-mon-ish (ad mən'ish, əd-) *vt.* [*ME amonesten* < *OFr amonester* < *ML *admonestare*, ult. < L *admonere* < *ad-*, to + *monere*, to warn] 1 to caution against specific faults; warn 2 to reprove mildly 3 to urge or exhort 4 to inform or remind, by way of a warning —*SYN.* ADVISE —**ad-mon-ish-ly** *adv.* —**ad-mon-ish-ment** *n.*

ad-mo-ni-tion (ad mō nish'ən) *n.* [*ME amonicioun* < *OFr amonition*, *admonition* < L *admonitio* < *admonere*; see prec.] 1 an admonishing, or warning to correct some fault 2 a mild rebuke; reprimand

ad-mon-i-tor (ad mən'it ər, əd-) *n.* [*< L admonere*; see ADMONISH] a person who admonishes

ad-mon-i-to-ry (-i tōrē) *adj.* admonishing; warning

ad-nate (ad nāt') *adj.* [*< L adnatus*, pp. of *adnasci*, to be born < *ad-*, to + *nasci*; see GENUS] Biol. congenitally joined together: said of unlike parts —**ad-na-tion** *n.*

ad-nau-se-am (ad nō'sē am', -zē-) [*L*, to nausea] to the point of disgust; to a sickening extreme

ad-nex-a (ad nek'sə) *n.pl.* [*ModL* < L, neut. pl. of *adnexus* < *adnectere*; see ANNEX] Anat. accessory parts or appendages of an organ (the ovaries are *adnexa* of the uterus) —**ad-nex'al** *adj.*

ado (ə dō) *n.* [*ME ado* < northern Eng dial. inf. at *do*, to do] fuss; trouble; excitement

ado-be (ə dō'bē) *n.* [*Sp* < *Ar at-tūba*, the brick < *al*, the + Coptic *tōbe*, brick] 1 unbaked, sun-dried brick 2 the clay of which such brick is made 3 a building made of adobe, esp. in the Southwest

ado-bo (ə dō'bō) *n.* a Philippine dish consisting of pork or chicken marinated in vinegar, garlic, soy sauce, etc., simmered, and then fried

ado-les-cence (ad' l es'ns) *n.* [*ME* & *OFr* < L *adolescencia* < *adolescens*; see fol.] 1 the state or quality of being adolescent 2 the time of life between puberty and maturity; youth

ado-les-cent (ad' l es'nt) *adj.* [*Fr* < L *adolescens*, prp. of *adolescere*, to come to maturity, be kindled, burn < **ad-adolescere* < *ad-*, to + *alescere*, to increase, grow up < *alere*, to feed, sustain; akin to OE *ald* (see OLD); Goth *alan*, to grow] 1 developing from childhood to maturity; growing up 2 of or characteristic of adolescence; youthful, exuberant, immature, unsettled, etc. —*n.* a boy or a girl from puberty to adulthood; teen-age person —*SYN.* YOUNG

Ad-olph (ad'əlf, ə dōlf) [*L Adolphus* < OHG *Adolf*, *Adulf*, lit., noble wolf < *adal*, nobility + *wolf*, WOLF] a masculine name; equiv. L *Adolphus*; Fr *Adolphe*; Ger *Adolf*

Ado-nai (ə dō nā'ē, -nī, -noī; ə dō nā'ī) [*Heb.* my Lord < NW Semitic *Adōn*, *Adun*, lord; ? (akin to Ar *ʔidhn*, command) God; Lord; used in Hebrew reading as a substitute for the "ineffable name" JHVH; see JEHOVAH

Ado-nis (ə dō nīs, -dān-) [*L* < Gr *Adōnis*] Gr. Myth. a handsome young man loved by Aphrodite; he is killed by a wild boar —*n.* any very handsome young man —**Adon'ic** (-dān'ik) *adj.*

adopt (ə dāpt') *vt.* [*L adoptare* < *ad-*, to + *optare*, to choose] 1 to choose and bring into a certain relationship; specif., to take into one's own family by legal process and raise as one's own child 2 to take up and use (an idea, a practice, etc.) as one's own 3 to choose and follow (a course) 4 to vote to accept (a committee report, motion, etc.) 5 to select as a required textbook —**adopt'able** *adj.* —**adopt'ee** *n.* —**adopt'er** *n.* —**adop-tion** *n.*

adop-tive (ə dāp'tiv) *adj.* [*L adoptivus*] 1 having to do with adoption 2 having become so by the act of adoption (adoptive parents) —**adop-tively** *adv.*

ador-able (ə dōr'ə bəl) *adj.* [*Fr* < L *adorabilis*] 1 [Now Rare] worthy of adoration or love 2 [Colloq.] delightful; charming; —**adorabil'ity** or **adorable-ness** *n.* —**ador'ably** *adv.*

ado-ra-tion (ad'ə rā'shən) *n.* [*Fr* < L *adoratio*] 1 a worshiping or paying homage, as to a divinity 2 great love, devotion, and respect

adore (ə dōr') *vt.* **adored**, **ador'ing** [*ME adouren* < *OFr adourer* < L *adorare*, to worship < *ad-*, to + *orare*, to speak; see ORATION] 1 to worship, as divine 2 to love greatly or honor highly; idolize 3 [Colloq.] to like very much —*SYN.* REVERE —**ador'er** *n.* —**ador-ingly** *adv.*

adorn (ə dōrn') *vt.* [*ME adornen* (altered after L) < *OFr aourner* < L *adornare* < *ad-*, to + *ornare*, to fit out; see ORNAMENT] 1 to be an ornament to; add beauty, splendor, or distinction to 2 to put decorations on; ornament

SYN. —**adorn** is used of that which adds to the beauty of something by gracing it with its own beauty (roses adorned her hair); **decorate** implies the addition of something to render attractive what would otherwise be plain or bare (to decorate a wall with pictures); **ornament** is used with reference to accessories which enhance the appearance (a crown ornamented with jewels); **embellish** suggests the addition of something highly ornamental or ostentatious for effect; to **beautify** is to lend beauty to, or heighten the beauty of; **bedeck** emphasizes the addition of showy things (bedecked with jewelry)

adorn-ment (ə dōrn'mənt) *n.* 1 an adorning or being adorned 2 a decoration or ornament

Ador-no (ə dōr'nō), Theodore Wie-sen-gründ (vē'zən groont') 1903-69; Ger. philosopher & music critic

Ado-wa (ad'ə wə, ad'-) *var.* of ADWA

ad-down (ə doun') *adv., prep.* [*ME adoun* < OE *adun*; see DOWN] 1 [Now Rare] down

ADP (ā'dē pē') [*a(denosine)-d(i)p(hosphate)*] a nucleotide, C₁₀H₁₆N₅O₁₀P₂, present in, and vital to the energy processes of, all living cells: during biological oxidations energy is stored in the ATP molecule as ADP is converted to ATP, which later converts back to ADP, releasing the energy needed for muscular contractions, photosynthesis, bioluminescence, biosynthesis, etc.

ADP *abbrev.* automatic data processing

Adras-tus (ə dras'tās) Gr. Myth. a king of Argos who leads the SEVEN AGAINST THEBES

ad-rem (ad' rem') [*L*, to (the) thing] dealing directly with the matter at hand; relevant

ad-re-nal (ə drē'nəl) *adj.* [*AD* + *RENAL*] 1 near the kidneys 2 of or from the adrenal glands —*n.* an adrenal gland

adrenal gland either of a pair of endocrine organs lying immediately above the kidney, consisting of an inner medulla which produces epinephrine and norepinephrine and an outer cortex which produces a variety of steroid hormones; see KIDNEY, ILLUS.

Adren-a-lin (ə dren'ə lin') [*ADRENAL* + *-IN*; so named (1901) by J. Takamine, U.S. chemist who first isolated it] trademark for EPINEPHRINE —*n.* [a-] epinephrine; also **adren-a-line** (ə dren'ə lin', -lən')

ad-re-ner-gic (ad'rē nur'jik) *adj.* [*< fol.* + Gr *erg(on)*, WORK + *-ic*] 1 releasing epinephrine or a similar substance (the adrenergic nerves of the sympathetic nervous system) 2 like epinephrine in chemical activity (an adrenergic drug)

ad-re-no- (ə drē'nō, -nā, -dren'ō, -dren'ə) *combining form* 1 adrenal glands [*adrenocortical*] 2 epinephrine [*adrenergic*] Also, before a vowel, **adren-**

adreno-chrome (ə drē'nō krōm', -nā, -dren'ō, -dren'ə) *n.* a red biochemical, C₉H₇NO₂, oxidized from epinephrine and having a hemostatic effect

ad-re-no-corti-cal (-kōr'ti kəl) *adj.* of, or produced in, the cortex of the adrenal glands

ad-re-no-corti-co-trop-ic (-kōr'ti kō'trəp'ik) *adj.* [*ADRENO-* + *CORTICO-* + *-TROPIC*] that can stimulate the cortex of the adrenal glands. Erroneously **ad-re-no-corti-co-troph'ic** (-trəf'ik)

adrenocorticotrophic hormone ACTH

Adria-my-cin (ā'drē ə mī'sin) trademark for a powerful antibiotic, C₂₇H₃₀ClNO₁₁, used intravenously to destroy cancerous tumors despite its potential serious side effects

Adri-an (ā'drē ən) [*L Adrianus*, *Hadrianus* < *Adria*, *Hadria*, name of two Italian cities] 1 a masculine name; fem. *Adrienne* 2 **Adrian IV** (born *Nicholas Breakspear*) c. 1100-59; pope (1154-59); the only Eng. pope 3 **Edgar Douglas** 1st Baron 1889-1977; Eng. neurophysiologist

Adri-an-o-ple (ā'drē ə nō'pəl) *old name* of EDIRNE

Adri-an-opo-lis (-nāp'ə lis) *ancient name* of EDIRNE

Adri-at-ic (Sea) (ā'drē at'ik) arm of the Mediterranean, between Italy and the Balkan Peninsula

Adri-enne (ā'drē ən', Fr ā drē ən') a feminine name; see ADRIAN

ad-ri-ft (ə drift') *adv., adj.* 1 floating freely without being steered; not anchored; drifting 2 without any particular aim or purpose

adroit (ə droit') *adj.* [*Fr* < *à*, to + *droit*, right < L *directus*, pp. of *dirigere*, DIRECT] skillful in a physical or mental way; clever; expert (his adroit handling of an awkward situation) —*SYN.* DEXTEROUS —**adroit'ly** *adv.* —**adroit'ness** *n.*

ad-sci-ti-tious (ad'si tish'əs) *adj.* [*< L adscitus*, pp. of *adsciscere*, to receive with knowledge, approve < *ad-*, to + *sciscere*, to seek to know < *scire*, to know; see SCIENCE] added from an external source; supplemental

ad-script (ad'skript') *adj.* [*L adscriptus*, pp. of *adscribere* < *ad-*, to + *scribere*, to write] written after

ad-scrip-tion (ad'skrip'shən) *n.* ADSRIPTION

ad-sorb (ad sōrb', -zōrb') *vt.* [*< AD-* + L *sorbere*; see ABSORB] to collect (a gas, liquid, or dissolved substance) in condensed form on a surface —**ad-sorb'able** *adj.*

ad-sorb-ate (ad sōr'bit, -zōr'bat') *n.* a gas, liquid, etc. taken up by adsorption

ad-sorb-ent (ad sōr'bənt, -zōr'-) *adj.* that is capable of adsorbing —*n.* a thing or substance that adsorbs

ad-sorp-tion (ad sōrp'shən, -zōrp'-) *n.* [*< ADSORB*, by analogy with ABSORPTION] an adsorbing or being adsorbed; adhesion of the molecules of a gas, liquid, or dissolved substance to a surface —**ad-sorp-tive** *adj.*

ad-suki bean (ad sō'ki, -zō'ki) ADZUKI BEAN

adu-lar-i-a (ə dō'ler ē ə, -jə) *n.* [*It* < Fr *adulaire*, after *Adula*, a group of mountains in Switzerland + *-aire*, *-ARY*] a translucent kind of orthoclase, as the moonstone

adu-late (ə dō'lat', -jə) *vt.* **-lat'ed**, **-lat'ing** [*< L adulatus*, pp. of *adulari*, to fawn upon, orig., to wag the tail < *ad-*, to + **ulos*, tail < IE **ulo* < base **wel-* > WALK; cf. WHEEL) 1 to praise too highly or flatter servilely 2 to admire intensely or excessively —**adu-la-tion** *n.* —**adu-la-tor** *n.* —**adu-la-to-ry** (-lə tōrē) *adj.*

adult (ə dult', ad'ult') *adj.* [*L adultus*, pp. of *adolescere*; see ADOLESCENT] 1 grown up; mature in age, size, strength, etc. 2 of or for adult persons (an adult novel) 3 containing or providing pornography (adult movies) —*n.* 1 a man or woman who is fully grown up; mature person 2 an animal or plant that is fully developed 3 a person who has reached the age of majority, now generally 18 years —*SYN.* RIPE —**adult'ness** *n.* —**adult'hood** *n.*

taining; composed of, or written in several languages.—*n.* 1 a person who speaks or writes several languages 2 a book written in several languages 3 a mixture or confusion of languages

Polygnotus (pāl'ig nō'təs) 5th cent. B.C.; Gr. painter

polygon (pāl'i gān) *n.* [*L. polygonum* < Gr. *polygōn*; neut. of *polygōnos*; see *POLY-* & *-GON*] a closed plane figure, esp. one with more than four sides and angles — **polygonal** (pāl'ig'ə-nəl) *adj.*

polygynous (pō lig'ə-nə; pō-) *n.* [*ModL* < *L. polygōnos* < Gr. *kind of plant, knotgrass* < *poly-*, many (see *POLY-*) + *gony*, a joint, KNEE; from the many joints] any of a genus (*Polygonum*) of annual or perennial plants of the buckwheat family, having conspicuous enlarged nodes, ocreae, and small whitish, greenish, or pink flowers in the leaf axils or in terminal clusters

polygraph (pāl'i graf) *n.* [*Gr. polygraphos*; writing much; see *POLY-* & *-GRAPH*] 1 an early device for reproducing writings or drawings 2 an instrument for recording simultaneously changes in blood pressure, respiration, pulse rate, etc.; see *LIE DETECTOR* — **polygraphically** *adv.*

polygyny (pō lig'ə-nē, pō-) *n.* [*< ModL. polygynia* < *POLY-* + Gr. *gynē*, woman, wife; see *GYN-*] 1 the state or practice of having two or more wives at the same time 2 Bot. the fact of having many styles or pistils 3 Zool. the mating of a male animal with more than one female — **polygynous** (pō lig'ə-nəs) *adj.*

polyhedron (pāl'i hē'drən) *n.* pl. **-drons** or **-dra** (-drā) [*ModL* < Gr. *polyedron*, neut. of *polyedros*; see *POLY-* & *-HEDRON*] a solid figure, esp. one with more than six plane surfaces; see also *PYRAMID*

polyhedral (pāl'i hē'drəl) *adj.* — **polyhedrally** *adv.*

polyhydric (pāl'i hi'drik) *adj.* [*POLY-* + *HYDR* (OXYL)]

containing more than one hydroxyl group (OH) in the molecule. Also **polyhydroxy** (-hi drak'sē)

Polyhymnia (pāl'i him'nē) [*L. < Gr. Polymnia*; *poly-*, *POLY-* + *hymnōs*, hymn; see *HYMN*] Gr. Myth. the Muse of sacred poetry. Also **Po-lym'nia** (pō lim'-)

polyimide (pāl'i i'mīd) [*poly-* (nasal) + *imide* (acid)] a synthetic

ribonucleic acid that promotes the production of interferon in the body

polymath (pāl'ə math) *n.* [*< Gr. polymathēs*, knowing much < *poly-*, *POLY-* + *mathanein*, learn; see *MATHEMATICAL*] a person of great and diversified learning — **polymathic** *adj.*

polymer (pāl'ə mār) *n.* [*Gr. polymēres*, of many parts; see *POLY-* & *-MEROS*] a naturally occurring or synthetic substance consisting of giant molecules formed from polymerization

polymerase (pāl'ə mār'ēz, -ās) *n.* any of various enzymes that promote polymerization; esp. of nucleic acids

polymeric (pāl'ə mēr'ik) *adj.* [*< Gr. polymerisch*; see *POLYMER*] of or relating to a polymer — **polymerically** *adv.*

polymerism (pō lim'ər iz'əm, pō; pāl'i mār-) *n.* the condition of being polymeric

polymerization (pō lim'ər ē zā'shən, pō; pāl'i mār-) *n.* 1 the process of chaining together many simple molecules to form a more complex molecule with different physical properties 2 the changing of a compound into a polymeric form by this process — **polymerize** (-iz', -ized', -iz'ing, vt., vi.)

polymorph (pāl'i mōrf) *n.* [*< Gr. polymorphos*; see *POLY-* & *-MORPH*] 1 Biol. a polymorphous organism or one of its forms 2 Chem. Mineralogy a substance that can crystallize in different forms 3 one of these forms

polymorphism (pāl'i mōr'fiz'əm) *n.* [*POLYMORPH(OUS)* + *-ISM*] 1 Chem. Mineralogy the property of certain substances of crystallizing in two or more different forms or systems 2 Biol. the condition in which a species has two or more very different morphological forms, as the castes of social insects or the flowers of certain plants

polymorphonuclear (pāl'i mōr'fō nōō'klē'ər, -nyōō-) *adj.* having a lobed nucleus, as the neutrophils

polymorphous (pāl'i mōr'fəs) *adj.* [*Gr. polymorphos*; see *POLY-* & *-MORPH*] of, having, or exhibiting polymorphism. Also **poly-morphously** *adv.*

polymyxin (pāl'i miks'in) *n.* [*< ModL. (Bacillus) polymyx(a)* (< *poly-*, *POLY-* + *myxa* < Gr. *myxa*, MUCUS) + *-IN*] any of various antibiotics obtained from strains of a soil bacterium (*Bacillus polymyxa*); esp. effective against Gram-negative bacteria

Polynesia (pāl'ē-nē'zhā, -shā) [*ModL* < Gr. *poly-*, *POLY-* + *nesos*, island] a major division of the Pacific islands east of the international date line, including Hawaii, Samoa, Tonga, the Society Islands, Marquesas Islands, etc.; cf. *MELANESIA*, *MICRONESIA*

Polynesian (pāl'i nē'zhān, -shān) *n.* 1 a member of any of the numerous peoples of Polynesia, including the Hawaiians, Tahitians, Samoans, Maoris, Marquesans, Tongans, and other groups 2 the languages of Polynesia, a subgroup of the Austronesian language family — **adj.** designating or of the Polynesians or their languages or cultures

polynuria (pāl'i nōō rit'is, -nyōō-) *n.* neuritis involving several nerves simultaneously

Polynices (pāl'i nī'sēz) [*Gr. Polyneikes*, lit., great wrangler < *polys*, many (see *POLY-*) + *neikos*, quarrel, akin to *Nikē*; see *NIKE*] Gr. a son of Oedipus and Jocasta; see *SEVEN AGAINST THEBES*

poly-nomial (pāl'i nō'mē əl) *n.* [*POLY-* + (BI)NOMIAL] an expression or name consisting of more than two terms; specif.: a) Algebra a linear combination of products of integral powers of a given set of variables with constant coefficients (Ex.: $x^2 + 3x + 2$ or $x^2 + 2xy + y^2$) b) Biol. a species or subspecies name consisting of more than two terms — **adj.** consisting of or characterized by polynomials

polynuclear (pāl'i nōō'klē'ər, -nyōō-) *adj.* [*POLY-* + *NUCLEAR*] having many nuclei. Also **polynuclearly** (-it) *adv.*

polynya (pāl'in'yā, pāl'in'yā) *n.* [*Russ. polyn'ya* < *polyn'*, hollow < Oslav. *pol-no-*, level area < *IE* base *plā-*, broad; flat] a PLANE, FLOOR

a usually oblong area of open water surrounded by sea ice

polyoma virus (pāl'ē ō'mē) [*POLY-* + *-OMA*] any of a genus (*Polyomavirus*) of DNA viruses that naturally infect wild and laboratory mice, and when injected into newborn mice or hamsters cause tumors

polyp (pāl'ip) *n.* [*Fr. polype* < *L. polypus* < Gr. *polypous* < *poly-*, *POLY-* + *pous*, foot] 1 any of various cnidarians, colonial or individual, having a mouth fringed with many small, slender tentacles bearing stinging cells at the top of a tubelike body, as the sea anemone or hydra 2 a smooth projecting growth of hypertrophied mucous membrane in the nasal passages, bladder, rectum, etc.

poly-paria (pāl'i pē'ri) *n.* pl. **-paries** [*ModL* < *L. polypus*, prec.] the common base or the connecting tissue to which each member of a colony of polyps is attached. Also **poly-parium** (-ē-əm), pl. **-ia** (-ē)

poly-peptide (pāl'i pep'tid) *n.* [*POLY-* + *PEPTIDE*] a substance containing two or more amino acids in the molecule joined together by peptide linkages

poly-petalous (pāl'i pet'ə-ləs) *adj.* [*POLY-* + *PETALOUS*] Bot. having separate petals

poly-phagous (pāl'i fā'jə, -jə) *n.* [*ModL* < Gr. *poly-*, *POLY-* + *phagēin*, to eat; see *PHAGOUS*] 1 excessive desire for food 2 the eating of or subsistence on many kinds of food — **polyphagous** (pō lif'ə-gəs) *adj.*

poly-phase (pāl'i fāz) *adj.* Elec. having, generating, or using alternating currents (usually three or a multiple of three) differing in phase (a *polyphase system*)

Polyphemus (pāl'i fē'məs) in Homer's *Odyssey*, a Cyclops who confines Odysseus and his companions in a cave until Odysseus blinds him so that they can escape

polyphemus moth (pāl'i fē'məs) a large, brownish American silk-worm moth (*Antheraea polyphemus*) with an eyelike spot on each hind wing

polyphone (pāl'i fōn) *n.* Phonet. a polyphonic letter or other symbol or a group of letters or symbols that is polyphonic

polyphonic (pāl'i fōn'ik) *adj.* [*Gr. polyphōnōs*, having many tones; see *POLY-* & *PHON*] 1 having or making many sounds 2 Music a) of or characterized by polyphony; contrapuntal b) that can produce more than one tone at a time, as a piano 3 Phonet. representing more than one sound, as the letter *c* as in *cat* and in *cereal*. Also **polyphonic** (pō lif'ə-nəs) — **polyphonically** *adv.*

polyphony (pō lif'ə-nē) *n.* [*Gr. polyphōnia*; see *POLY-* & *PHONY*] 1 multiplicity of sounds, as in an echo 2 Music a combining of a number of independent but harmonizing melodies, as in a fugue or canon; counterpoint 3 Phonet. the representation of two or more sounds by the same letter, symbol, or group of symbols, as the group *ath* as in *then* and in *thin*

polyphyletic (pāl'i fī'let'ik) *adj.* [*POLY-* + *PHYLETIC*] Biol. derived from more than one ancestral type — **polyphyletically** *adv.*

polypide (pāl'ip'id, -id') *n.* [*POLY-* + *IDE* (var. of *ID*)] Zool. (sense 2) any of the polypoid forms

polyploid (pāl'i ploid) *adj.* [*POLY-* + *-PLOID*] having the number of chromosomes in the somatic cells three or more times the haploid number — *n.* a polyploid cell or organism — **polyploidy** *n.* [*Gr. polyploidia* < *Gr. polyploidia* < *poly-*, *POLY-* + *ploidia* (gen. *pōidos*); foot; from its creeping rootstocks] any of a genus (*Polypodium*; family Polypodiaceae) of ferns with leathery pinnatifid leaves borne on creeping rootstocks

polypous (pāl'ip'əs) *adj.* of or like a polyp

polypropylene (pāl'i prō'pā-lēn') *n.* [*POLY(MER)* + *PROPYLENE*] polymerized propylene; a very light, highly resistant, thermoplastic resin used in packaging, coating, pipes and tubes, etc.

polyptych (pāl'ip'tik) *n.* [*Gr. polyptychos*, having many folds < *poly-* (see *POLY-*) + *ptyx*, a fold] a set of four or more panels with pictures, carvings, etc. often hinged for folding together, used as an altarpiece, etc.

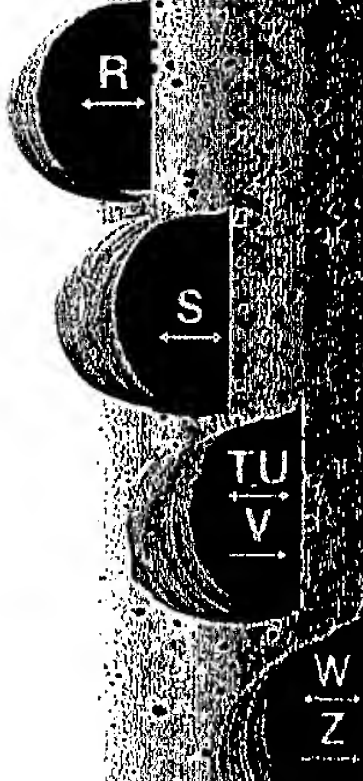
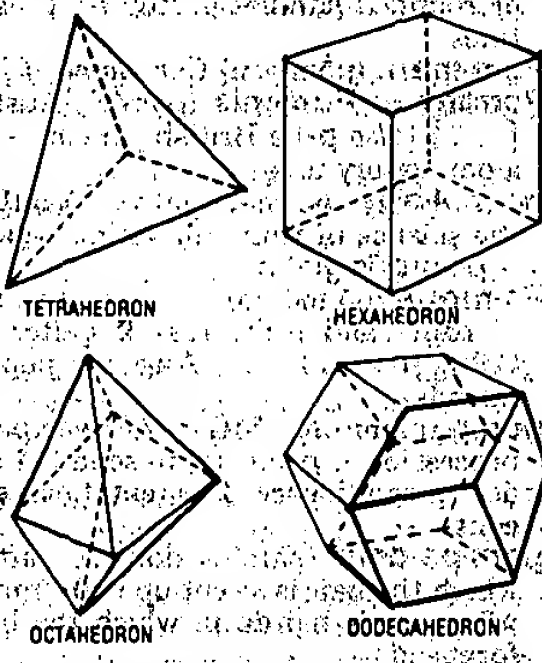
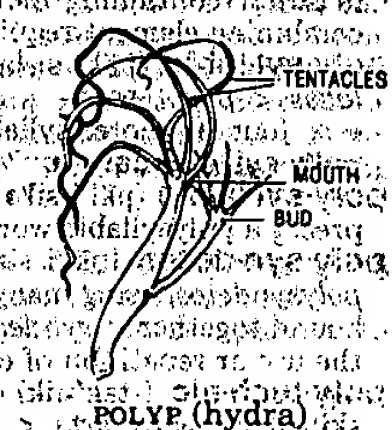
polyrhythm (pāl'i ruh'əm) *n.* [*POLY-* + *RHYTHM*] Music 1 the use of strongly contrasting rhythms in simultaneous voice parts 2 such a rhythm usually used in pl. — **polyrhythmic** *adj.*

polyribose (pāl'i ri'bō-sōm') *n.* POLYSOME

polysaccharide (pāl'i sak'ə-rid) *n.* [*POLY-* + *SACCHARIDE*] any of a group of complex carbohydrates, as starch, that decompose by hydrolysis into a large number of monosaccharide units

at, ate, car, ten, eve, is, ice, gō, hōrn, look, tool, oil, but, up, far, a for unstressed vowels, as a in ago, u in focus, as in Latin (lat'n); chin, she, zhā in azure (az'hər); thin, the, n as in ring (rīn) In etymologies: * = unattested; < = derived from; > = from which

* = Americanism; & = & See inside front and back covers



Physical Chemistry of Surfaces

Fifth Edition

ARTHUR W. ADAMSON

*Department of Chemistry, University of Southern California
Los Angeles, California*



A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons, Inc.

NEW YORK / CHICHESTER / BRISBANE / TORONTO / SINGAPORE

Copyright © 1990 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Sections 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Adamson, Arthur W.

Physical chemistry of surfaces/Arthur W. Adamson.—5th ed.
p. cm.

“A Wiley-Interscience publication.”

Includes bibliographical references.

ISBN 0-471-61019-4

1. Surface chemistry. 2. Chemistry, Physical and theoretical.

I. Title.

QD506.A3 1990

90-12106

541.3'3—dc20

CIP

Printed in the United States of America

10 9 8 7

CHAPTER XI

The Solid-Liquid Interface—Adsorption from Solution

This chapter on adsorption from solution is intended only to develop the more straightforward and important aspects of adsorption phenomena that prevail when a solvent is present. The general subject has a vast literature, and it is both necessary and reasonable in a textbook to limit the presentation to the more important characteristic features and theory.

With nonelectrolytes, a logical division is made according to whether the adsorbate solution is dilute or concentrated. In the first case treatment is very similar to that for gas adsorption, whereas in the second case the role of solvent becomes more explicit. The adsorption of electrolytes is treated briefly, mainly in terms of the exchange of components in an electrical double layer either at the surface of a nonporous particle or in an ion exchanger or zeolite.

A very important application of adsorption phenomena is that of chromatography, where the adsorbed material is held in a fixed bed or conformation, and solution passes down its length; alternatively, the solution may travel or spread along a thin film of adsorbent. Some aspects relating to adsorption affinities are mentioned in Section XI-1B.

1. Adsorption of Nonelectrolytes from Dilute Solution

The adsorption of nonelectrolytes at the solid-solution interface may be viewed in terms of two somewhat different physical pictures. The first is that the adsorption is essentially confined to a monolayer next to the surface, with the implication that succeeding layers are virtually normal bulk solution. The picture is similar to that for the chemisorption of gases (see Chapter XVII) and similarly carries with it the assumption that solute-solid interactions decay very rapidly with distance. Unlike the chemisorption of gases, however, the heat of adsorption from solution is usually fairly small and is more comparable with heats of solution than with chemical bond energies.

The second picture is that of an interfacial layer or region, multimolecular in depth (perhaps even 100 Å deep), over which a more slowly decaying interaction potential with the solid is present (note Section X-6C). The situa-

tion would then be more like that in the physical adsorption of vapors (see Chapter XVI), which become multilayer near the saturation vapor pressure (e.g., Fig. X-16). Adsorption from solution, from this point of view, corresponds to a partition between a bulk and an interfacial phase; the Polanyi potential concept may be used (see Section XI-1C).

While both models find some experimental support, the monolayer one has been much the more amenable to simple analysis. As a consequence, most of the discussion in this chapter is in terms of it, although occasional *caveats* are entered. We consider first the case of adsorption from dilute solution, as this corresponds to the usual experimental situation and also because the various adsorption models take on a simpler algebraic form and are thus easier to develop than those for concentrated solutions.

A. Adsorption Isotherms

The moles of solute species adsorbed per gram of adsorbent is given experimentally by $\Delta C_2 V_{\text{sol}}/m$, where ΔC_2 is the change in concentration of the solute following adsorption, V_{sol} is the total volume of solution, and m is the grams of adsorbent. It will be convenient in the following development to suppose that mole numbers and other extensive quantities are on a *per gram of adsorbent basis*, so that n_2^s , the moles of solute adsorbed per gram, is given by

$$n_2^s = V \Delta C_2 = n_0 \Delta N_2 \quad (\text{XI-1})$$

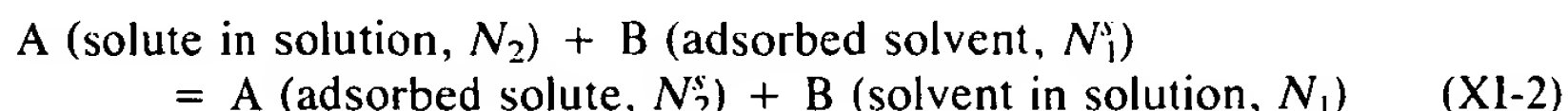
where n_0 is the total moles of solution per gram of adsorbent and ΔN_2 is the change in mole fraction of solute following adsorption. In dilute solution, both forms are equivalent, although, as seen in Section XI-4, this is not the case otherwise. See the discussion of definitions and terminology by Everett (1, 3) and Schay (2); n_2^s has been called the *specific reduced surface excess*, for example.

The quantity n_2^s is in general a function of C_2 , the equilibrium solute concentration, and temperature for a given system, that is, $n_2^s = f(C_2, T)$. At constant temperature, $n_2^s = f_T(C_2)$, and this is called the *adsorption isotherm function*. The usual experimental approach is to determine this function, that is, to measure adsorption as a function of concentration at a given temperature. See Ref. 5 for a discussion of experimental methods.

Various functional forms for f have been proposed either as a result of empirical observation or in terms of specific models, and a particularly important example of the last is that known as the *Langmuir* adsorption equation (4). By analogy with the derivation for the case of gas adsorption (see Section XVI-3), the Langmuir model assumes the surface to consist of adsorption sites, the area per site being σ^0 ; all adsorbed species interact only with a site and not with each other, and adsorption is thus limited to a monolayer. There are related lattice models, as in Ref. 5. In the case of adsorption from solution, however, it seems more plausible to consider an alternative phrasing of the model. Adsorption is still limited to a monolayer,

but this layer is now regarded as an ideal two-dimensional solution of equal size solute and solvent molecules of area σ^0 . Thus lateral interactions, absent in the site picture, cancel out in the ideal solution layer picture because of being independent of composition. However, in the first version σ^0 is a property of the solid lattice, while in the second it is a property of the adsorbed species; both versions attribute differences in adsorption behavior entirely to differences in adsorbate-solid interactions. Both present adsorption as a competition between solute and solvent. See Ref. 6 for a discussion of types of adsorption forces.

It is perhaps fortunate that both versions lead to the same algebraic formulations, but we will imply a preference for the two-dimensional solution picture by expressing surface concentrations in terms of mole fractions. The adsorption process can now be written as



The equilibrium constant for this process is

$$K = \frac{N_2^s a_1}{N_1^s a_2} \quad (\text{XI-3})$$

where a_1 and a_2 are the solvent and solute activities in solution and, by virtue of the model, the activities in the adsorbed layer are given by the respective mole fractions N_1^s and N_2^s . Since the treatment is restricted to dilute solutions, a_1 is constant, and we can write $b = K/a_1$; also, $N_1^s + N_2^s = 1$ so that Eq. XI-3 becomes

$$N_2^s = \frac{b a_2}{1 + b a_2} \quad (\text{XI-4})$$

Since $n_2^s = N_2^s n^s$, where n^s is the number of moles of adsorption sites per gram, Eq. XI-3 can also be written

$$n_2^s = \frac{n^s b a_2}{1 + b a_2} \quad (\text{XI-5})$$

or

$$\theta = \frac{b a_2}{1 + b a_2}$$

where $\theta = n_2^s/n^s$ is the fraction of surface occupied. Also,

$$n^s = \frac{\Sigma}{N \sigma^0} \quad (\text{XI-6})$$

where Σ denotes the surface area per gram. In sufficiently dilute solution, activity coefficient effects will be unimportant, so that in Eq. IX-4, a_2 may be replaced by C_2 .

The equilibrium constant K can be written

$$K = e^{\Delta S^0/R} e^{-\Delta H^0/RT} \quad (\text{XI-7})$$

where ΔH^0 is the net enthalpy of adsorption, often denoted by $-Q$, where Q is the heat of adsorption. Thus the constant b can be written

$$b = b' e^{Q/RT} \quad (\text{XI-8})$$

The entropies and enthalpies of adsorption may be divided, in a formal way, into separate quantities for each component:

$$K = \frac{K_2}{K_1} \quad \Delta S^0 = \Delta S_2^0 - \Delta S_1^0 \quad \Delta H^0 = \Delta H_2^0 - \Delta H_1^0 \quad (\text{XI-9})$$

It is not necessary to limit the model to that of idealized sites; Everett (7) has extended the treatment by incorporating surface activity coefficients as corrections to N_1^s and N_2^s . ΔH^0 may be calculated from the temperature dependence of the adsorption isotherm (8). If the solution is taken to be ideal,

$$\left(\frac{\partial \ln C}{\partial T} \right)_n = - \frac{\Delta H^0}{RT^2} \quad (\text{XI-10})$$

(note Eq. XVI-116).

Returning to Eq. XI-4, with C_2 replacing a_2 , at low concentrations n_2^s will be proportional to C_2 , with a slope $n^s b$. At sufficiently high concentrations, n_2^s approaches the limiting value n^s . Thus n^s is a measure of the capacity of the adsorbent and b of the intensity of the adsorption. In terms of the ideal model, n^s should not depend on temperature, while b should show an exponential dependence, as given by Eq. XI-8. The two constants are conveniently evaluated by putting Eq. XI-5 in the form

$$\frac{C_2}{n_2^s} = \frac{1}{n^s b} + \frac{C_2}{n^s} \quad (\text{XI-11})$$

That is, a plot of C_2/n_2^s versus C_2 should give a straight line of slope $1/n^s$ and intercept $1/n^s b$.

An equation algebraically equivalent to Eq. XI-4 results if instead of site absorption the surface region is regarded as an interfacial solution phase, much as in the treatment in Section III-7C. The condition is now that $v^s = n_1^s \bar{V}_1 + n_2^s \bar{V}_2$. If a_1^s and a_2^s , the activities of the two components in the

interfacial phase, are represented by the volume fractions V_1^s and V_2^s , the result is

$$v_2^s = \frac{v^s b a_2}{1 + b a_2} \quad (\text{XI-12})$$

Here v_2^s is the volume of absorbed solute, and v^s is the (constant) volume of the interfacial solution (9).

Most surfaces are heterogeneous so that b in Eq. XI-8 will vary with θ . The adsorption isotherm may now be written

$$\Theta(C_2, T) = \int_0^\infty f(b) \theta(C_2, b, T) db \quad (\text{XI-13})$$

where $f(b)$ is the distribution function for b , $\theta(C_2, b, T)$ is the adsorption isotherm function (e.g., Eq. XI-5), and $\Theta(C_2, T)$ is the experimentally observed adsorption isotherm. In a sense, this approach is an alternative to the use of surface activity coefficients.

The solution to this integral equation is discussed in Section XVI-15, but one particular case is of interest here. If $\theta(C_2, b, T)$ is given by Eq. XI-5 and the variation in b and θ is attributed entirely to a variation in the heat of adsorption Q and $f(Q)$ is taken to be

$$f(Q) = \alpha e^{-Q/nRT} \quad (\text{XI-14})$$

then the solution to Eq. XI-13 is of the form (10, 11)

$$\Theta = \frac{n_2^s}{n^s} = a C_2^{1/n} \quad (\text{XI-15})$$

where $a = \alpha R T n b'$ and b' is as defined in Eq. XI-8. Equation XI-15 is known as the *Freundlich adsorption isotherm* after its user (12). See Ref. 13 for representative values of a and n for aqueous organic solutes adsorbed on activated carbons.

The Freundlich equation, unlike the Langmuir, does not become linear at low concentrations but remains convex to the concentration axis; nor does it show a saturation or limiting value. The constants $(a n^s)$ and n may be obtained from a plot of $\log n_2^s$ versus $\log C_2$, and roughly speaking, the intercept $a n^s$ gives a measure of the adsorbent capacity and the slope $1/n$ of the intensity of adsorption. As just mentioned, the shape of the isotherm is such that n is a number greater than unity.

There is no assurance that the derivation of the Freundlich equation is unique; consequently, if data fit the equation, it is only likely, but not proven, that the surface is heterogeneous—see Problem 1 for an alternative interpretation! Basically, the equation is an empirical one, limited in its usefulness to its ability to fit data.

Alternative approaches treat the adsorbed layer as an ideal solution or in terms of a Polanyi potential model (see Refs. 13a, 13b, and 14 and Section XVI-7). A related

approach has been expounded by Myers and Sircar (14a). Adsorption may be affected by polarization of the adsorbed layer (15). Adsorption *rates* have been modeled as diffusion controlled (16, 17).

B. Qualitative Results of Adsorption Studies—Traube's Rule

The nonelectrolytes that have been studied are for the most part organic compounds; these include fatty acids, aromatic acids, esters, and other single functional group compounds plus a great variety of more complex species such as porphyrins, bile pigments, carotenoids, lipids, and dyestuffs. Frequently these more complex substances have been studied only in terms of their chromatographic behavior, so that qualitative information concerning relative adsorbabilities may be known but not actual isotherms.

Typical adsorbents, especially of the older literature, include alumina, silica gel, various forms of carbon (blood charcoal, sugar charcoal, etc., and carbon blacks), and various organic compounds such as sugars and starches. In the case of hydrous oxides and carbons, not only are the composition and state of subdivision important, but also the adsorptive properties are strongly dependent on the moisture content and degree of heating or activation used. As to solvents, a great deal of work has been done with aqueous systems, but since organic absorbates are common, one also finds data for solutions in a variety of common organic solvents.

The behavior of a given system may be predicted very qualitatively in terms of the separate adsorption constants of Eqs. XI-9. The rule is that a polar (nonpolar) adsorbent will preferentially adsorb the more polar (nonpolar) component of a nonpolar (polar) solution. Polarity is used here in the general sense of ability to engage in hydrogen bonding or dipole-dipole type interactions as opposed to nonspecific dispersion interactions. A semiquantitative extension of the foregoing is known as Traube's rule (18), which, as given by Freundlich (8), states: "The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series."

Data illustrating Traube's rule are shown in Fig. XI-1a, in which it is seen that the initial slopes, and hence *b* values in Eq. XI-4, increase in the order formic acid, acetic acid, propionic acid, and butyric acid. The adsorption in this case was on carbon and from aqueous solution. Holmes and McKelvey (19) made the logical extension of Freundlich's statement by noting that the situation really is a relative one and that a reversal of order should occur if a polar adsorbent and a nonpolar solvent were used. Thus as illustrated in Fig. XI-1b, the reverse sequence was indeed observed for fatty acids adsorbed on silica gel from toluene solution. There is a large current literature; some useful citations are Refs. 20-25.

As discussed in Chapter III, the uniform progression in adsorbabilities in proceeding along a homologous series can be understood in terms of a constant increment in the work of adsorption with each additional CH₂ group.

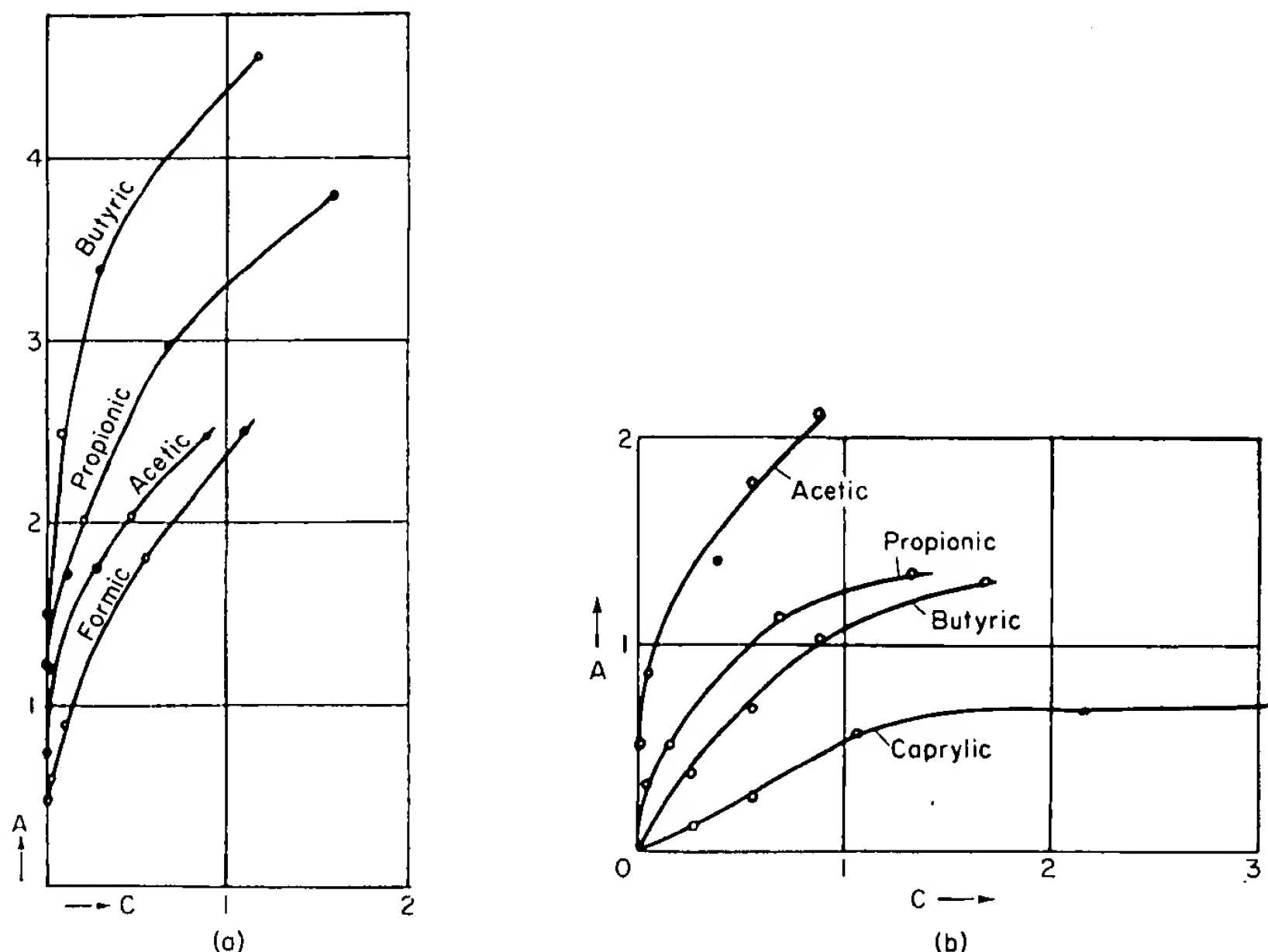


Fig. XI-1. Illustration of Traube's rule: (a) adsorption of fatty acids on carbon from aqueous solution; (b) adsorption of fatty acids on silica gel from toluene. (From Ref. 18.)

The film pressure π may be calculated from the adsorption isotherm by means of Eq. X-11 as modified for the case of adsorption from a dilute solution:

$$\pi = \frac{RT}{\Sigma} \int_0^{C_2} n_2^s d \ln C_2 \quad (\text{XI-16})$$

If the Langmuir equation is obeyed, then combination of Eqs. XI-5, XI-6, and XI-16 gives

$$\pi = \frac{RT}{N\sigma^0} \ln(1 + bC_2) \quad (\text{XI-17})$$

so that equal values of bC_2 correspond to equal values of π . Eq. XI-17 is known as the *Szyszkowski* equation (26). The sequence shown in Fig. XI-1a may thus be interpreted as meaning that as the homologous series is ascended, successively lower concentrations suffice to give the same film pressure. This last statement is now entirely parallel to the usual form of Traube's rule as applied to the surface tension of solutions (Section III-7E).

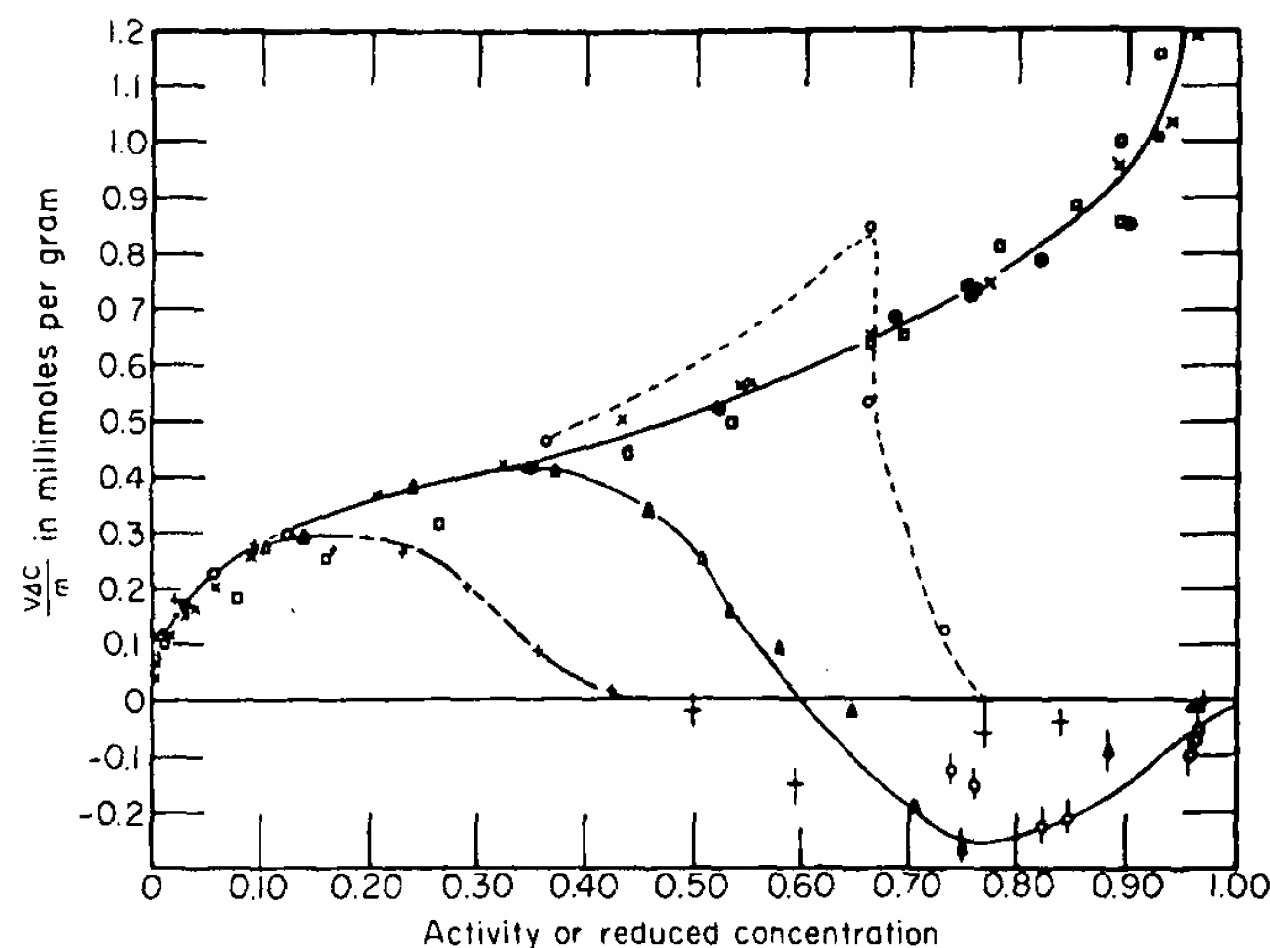


Fig. XI-2. Adsorption of fatty acids on Spheron 6: +, acetic; Δ , propionic; \circ , *n*-butyric; \times , *n*-valeric; \bullet , *n*-caproic; \square , *n*-heptylic. (From Ref. 28.)

Interestingly, π may also be calculated from the variation of zeta potential with amount adsorbed (see Ref. 27).

Another observation is that there is generally an inverse relationship between the extent of adsorption of a species and its solubility in the solvent used, that is, the less soluble the material, the more strongly will it tend to be adsorbed. For example, Hansen and Craig (28) found that the adsorption isotherms of members of a homologous series of fatty acids or alcohols were superimposable on each other if plotted as grams adsorbed per gram of adsorbent versus the *reduced concentration* C_2/C_2^0 . Here, C_2^0 denotes the solubility of the adsorbate in the solvent. The adsorbents used were Graphon and Spheron, the former being a rather uniform surface carbon obtained by partial graphitization of carbon black, and the solvent was water. A similar superimposability is observed in the adsorption of vapors (see Section XVI-9). One of Hansen and Craig's plots is shown in Fig. XI-2; the deviations of the lower members at high C_2/C_2^0 values stem from the fact that their solubilities were rather high so that a secondary effect, discussed in Section XI-4, was present.

The correlating role of C_2^0 provides emphasis to the view of adsorption as a partition between the solution and interfacial phases; K_1 and K_2 in Eq. XI-9 can be regarded as the separate partition coefficients. Thus, a good solvent affects ΔS_2 and ΔH_2 so as to reduce K_2 , and qualitatively, $K_2 C_2^0$ tends to be a constant. The effect of increasing temperature, which is usually to decrease the adsorption, that is, to decrease b or K in Eq. XI-9, can be understood either in terms of adsorption normally being exoergic or in terms of the preceding, as reflecting an increase in C_2^0 . For example, Bartell (28a) found that although the adsorption of *n*-butyl alcohol on charcoal from dilute solutions increased with temperature, the reverse dependence developed with more concentrated solutions. This reversal was attributed to the decreasing solubility of butyl alcohol in water with increasing temperature.

There is an effect on K of high pressure (several thousand atmosphere range). In the case of $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ adsorbing on TiO_2 (anatase) from acetonitrile solution, the pressure effect corresponded to a partial molal volume change on adsorption of about $7 \text{ cm}^3/\text{mol}$ (29).

The preceding discussion helps to underline the point that adsorption from solution is a relatively complex phenomenon; it depends on the nature of solute-solvent interactions in the solution phase and in the interfacial region as well as on their interactions with the adsorbent. It therefore can be appreciated that it is difficult to be very much more specific on constitutive effects than in the discussion of Traube's rule. However, generally speaking, the adsorption constant K can be expected to be large if there is a specific opportunity for adsorbent-adsorbate hydrogen bonding. Kipling (30) cites as examples the relative affinities of silica gel for a series of nitro and nitroso derivatives of diphenylamine and *N*-ethylaniline (31) and the much stronger adsorption of phenol on charcoal than of the diorthotertiarybutyl derivative (32). It should be noted that many charcoals have partially oxidized surfaces. Thus Spheron 6, which has surface oxygens (33), adsorbs alcohol preferentially over benzene, but after heating at 2700°C (to give Graphon), it prefers benzene (34). Aromatic ring compounds tend to adsorb preferentially to aliphatic ones, for example, on carbon, presumably because of π electron interactions or, alternatively, because of the higher polarizability of such rings. Bulky substituents reduce this preference, perhaps because of their preventing a close approach of the ring to the adsorbent surface (32). High-molecular-weight materials such as sugars, dyes, and polymers tend to be more strongly adsorbed than low-molecular-weight species. In chromatography the order of elution is normally inverse as the K value for adsorption so that even the qualitative literature provides a host of comparisons.

Purely geometric effects apparently can be important in that Linde molecular sieve 5\AA adsorbs hexane preferentially to benzene presumably because only the former can pass into the pores; the large pore size 10- and 13- \AA sieves show much stronger adsorption of benzene (35). Quite apart from such specific effects, it has been speculated that the fundamental mechanism of adsorption in a porous solid may be more akin to capillary condensation (see Section XVI-16B) than to surface adsorption. Hansen and Hansen (36) have supported this point of view; the picture would be one of relatively thick pockets of adsorbed phase held by virtue of a low solution-adsorbed phase-solid contact angle and a finite adsorbed phase-solution interfacial tension. This is a definite possibility in the case of systems near a solubility limit (see Section XI-1C), but as a general explanation this mechanism has been argued against fairly effectively (9, 37).

Finally, the adsorbent-adsorbate interaction may be so specific that the adsorption may properly be called chemisorption; the isotherm will tend to be of the simple Langmuir type, with a very large K value, and adsorption may be slow. The adsorption of fatty acids on metals is often of this type, probably due to salt formation with the oxide coating of the metal. Thus

Hackerman and co-workers (38) found that fatty acids, nitriles, and so forth, showed a partially irreversible adsorption on iron and steel powder, obeying the Langmuir isotherm, while Smith and Allen (39) noted that the adsorption of *n*-nonadecanoic acid on copper, nickel, iron, and aluminum was quite dependent on whether the surface used had been exposed by machining in air or under solvent, away from oxygen. Whitesides and co-workers (40) used a variety of physical and spectroscopic methods to determine that highly organized structures were present in films of organosulfur compounds adsorbed onto gold surfaces. Similar studies have been made by Allara and co-workers (41).

C. Multilayer Adsorption

Equation XI-5, the Langmuir equation, applies to a large number of adsorption systems where dilute solutions are involved, but some interesting cases of sigmoid isotherms have been reported. Hansen et al. (42) found that for a number of higher acids and alcohols (four or more carbon atoms) adsorbed on various carbons from aqueous solution, the isotherms showed no saturation effect but rather the general shape characteristic of multilayer adsorption (see Section XVI-5). The final, marked increase in adsorption took place, significantly, as the saturation concentration was approached.

It is appealing to accept the parallel to low-temperature gas adsorption where, after a semiplateau region in the isotherm plot, one finds rapidly increasing adsorption occurring as the saturation pressure P^0 is approached. With such gas adsorption isotherms, the rational variable is the reduced pressure P/P^0 , in the case of solution adsorption, it was noted in the preceding section that C/C^0 is the correlating variable. Some of the data reported by Hansen et al. are shown in Fig. XI-2. There seems to be no doubt that some form of multilayer adsorption was occurring; otherwise, impossibly small areas per molecule would be implied.

In solution adsorption, two potentially adsorbing components must be present, unlike the case with gas adsorption, and there is really no good reason to suppose that multilayer adsorption of a solute occurs with complete exclusion of solvent. In other words, the situation might more profitably be regarded as one of a phase separation induced by the interactions with the solid surface or as a capillary effect. As a potential example of the first case, Kiselev and co-workers (43) found a sigmoid isotherm for the adsorption of methanol in heptane by silica gel that rose to very high values as C_2/C_2^0 approached unity. On the other hand, Bartell and Donahue (44) reported isotherms for the adsorption of water by silica gel from solutions in hexyl alcohol in which the rapid terminal increase in adsorption took place at C_2/C_2^0 values around 0.8. Such behavior is characteristic of capillary condensation in the case of gas adsorption, and it is possible here that a capillary-induced phase separation occurred. Since water is preferentially adsorbed, there would be a tendency, with increasing concentration, for a water-rich layer to deepen and to go over to meniscus formation in a pore if the capillary pressure from the resulting curvature provided a positive driving force. This would be the case if the effect of the pressure were to make the local value of C_2^0 smaller.

A perhaps simpler type of multilayer formation is that in which physical adsorption of a species occurs on top of its own chemisorbed layer. The observed isotherm

may then be a sum of two Langmuir isotherms, but if the chemisorption is complete at a low concentration, the effect is that of an isotherm that is ordinary in appearance except that it originates from a point a way up on the adsorption axis of the isotherm plot. Behavior of this type was observed in the adsorption of caproic and stearic acids on steel (45). While this interpretation is plausible in the case cited, the same behavior could in principle result from the presence of two kinds of surface, one much more strongly adsorbing than the other.

2. Adsorption of Polymers

The study of adsorption of polymers is so interwoven with the general field of polymer chemistry, and hence so relatively specialized, that only a brief summary presentation is attempted here. First, the requirement that the polymer be soluble limits solution adsorption studies mainly to linear macromolecules. These include synthetic rubber polymers, cellulose-type polymers, and methacrylate, vinyl, styrene, and so on, polymers, mostly in fairly polar organic solvents and mostly with carbon as the adsorbent (perhaps because of the bias of the rubber industry). See Refs. 30 and 47 to 49 for reviews. A second point is that polymers as prepared are generally polydisperse, and their adsorption is more that of a multicomponent system in which fractionation effects can be important. The more recent work has stressed the use of at least relatively narrow molecular weight fractions. Third, as was true at the water-air interface (Section IV-11), a large number of configurations at the solid-solution interface are possible, and probably for this reason adsorption equilibrium can be exceedingly slow in attainment; adsorption that appears to have leveled off after an hour or two may actually be subject to continued drift upward for days or months (note Ref. 48). Heller (50) gives the equation

$$\frac{t}{x/m} = k + k't \quad (\text{XI-18})$$

where x/m is grams adsorbed per gram of adsorbent and t is time. Fourth, it takes several parameters to describe the state of a polymer at an interface. These include the number of points of attachment, the horizontal spread as given by the average radius $(\bar{r}^2)^{1/2}$, and the thickness Δr , as illustrated in Fig. XI-3. There are, in fact, more parameters than realistically can be extracted from adsorption data, and this has made it difficult to confirm or deny the various proposed models.

A very simple model is that derived from the mass action approach in which Eq. XI-2 is modified by writing that v molecules of solvent are displaced per polymer molecule. This introduces $(N_1)^v$ so that we have (51)

$$\frac{\theta}{v(1 - \theta)^v} = bC_2 \quad (\text{XI-19})$$

Next, it is possible to introduce various assumptions concerning the adsorption statistics, for example, that there is a Gaussian distribution of end-to-end distances. An approach of this type led to the equation (52)

$$\frac{\theta}{(1 - \theta)e^{2Kz_0}} = (KC)^{1/v} \quad (\text{XI-20})$$

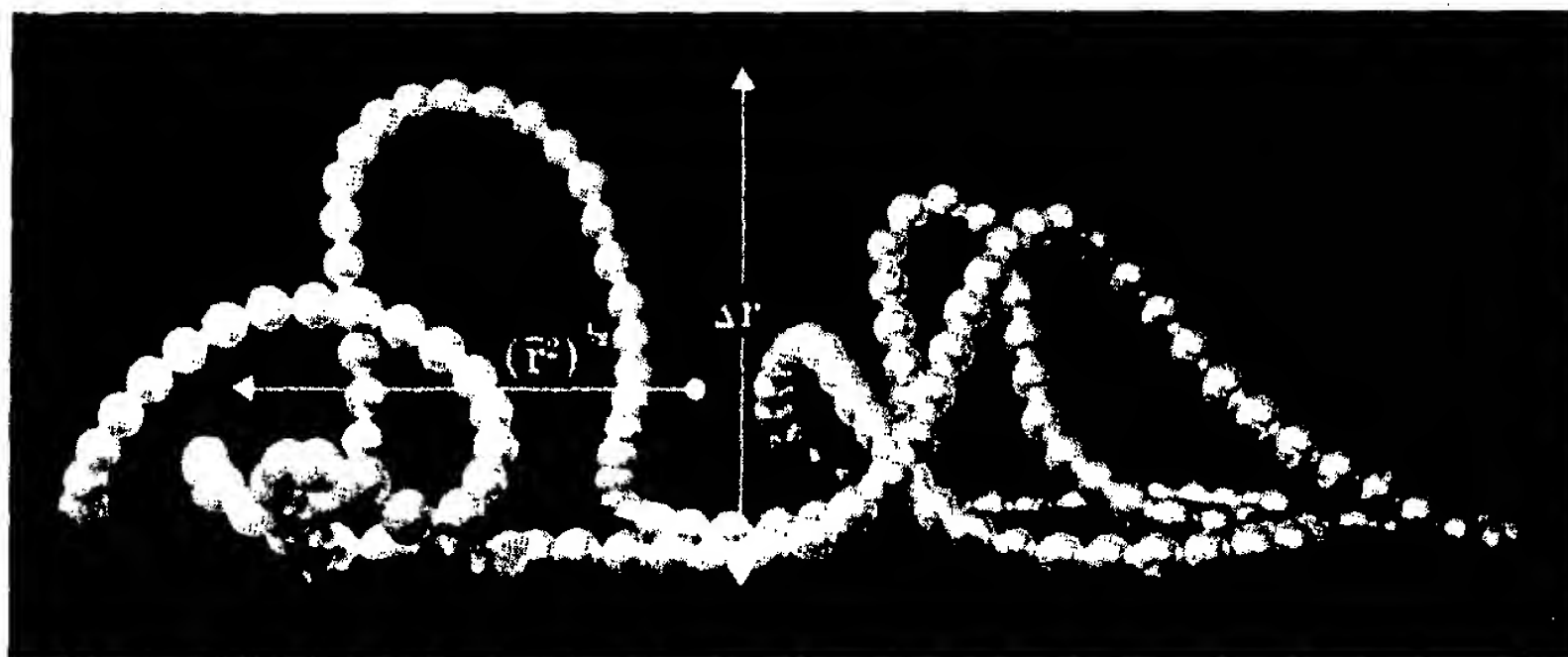


Fig. XI-3. Hypothetical conformation of an adsorbed chain molecule. (From Ref. 47.)

A number of more detailed approaches have been made. Treatments based on a lattice model include those of Silberberg (53), Hove (54), Roe (55), and Sheutjens and Fler (56). Random-walk approaches include those of Simha (57) and Rubin and Dimarzio (58). Statistical approaches are those of Everett and co-workers (59), Frisch (60), and de Gennes (61). Gast (61a) proposes various scaling relationships. In view of the sophistication of the various treatments, it is almost embarrassing that most polymer adsorption data fit the simple Langmuir Equation, Eq. XI-5, as well as any other, within experimental error (see Refs. 50, 62).

Representative adsorption isotherms are shown in Fig. XI-4. The situation is sufficiently complex in the case of polymers that an analysis of why the mass action

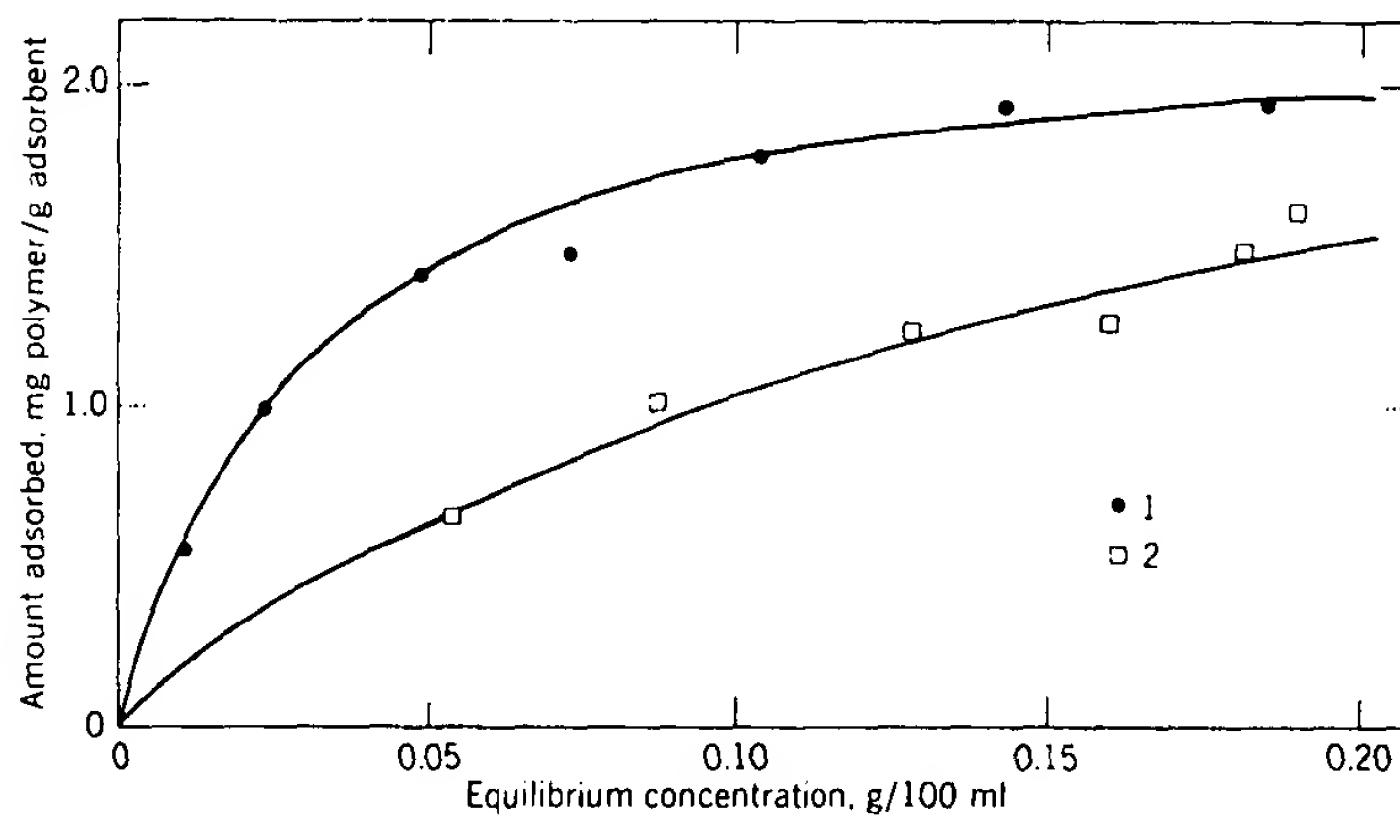


Fig. XI-4. Adsorption of polystyrene from benzene onto pyrex glass at 30°C. Curve 1: polymer molecular weight 950,000; curve 2: polymer molecular weight 110,000. (From Ref. 63.)

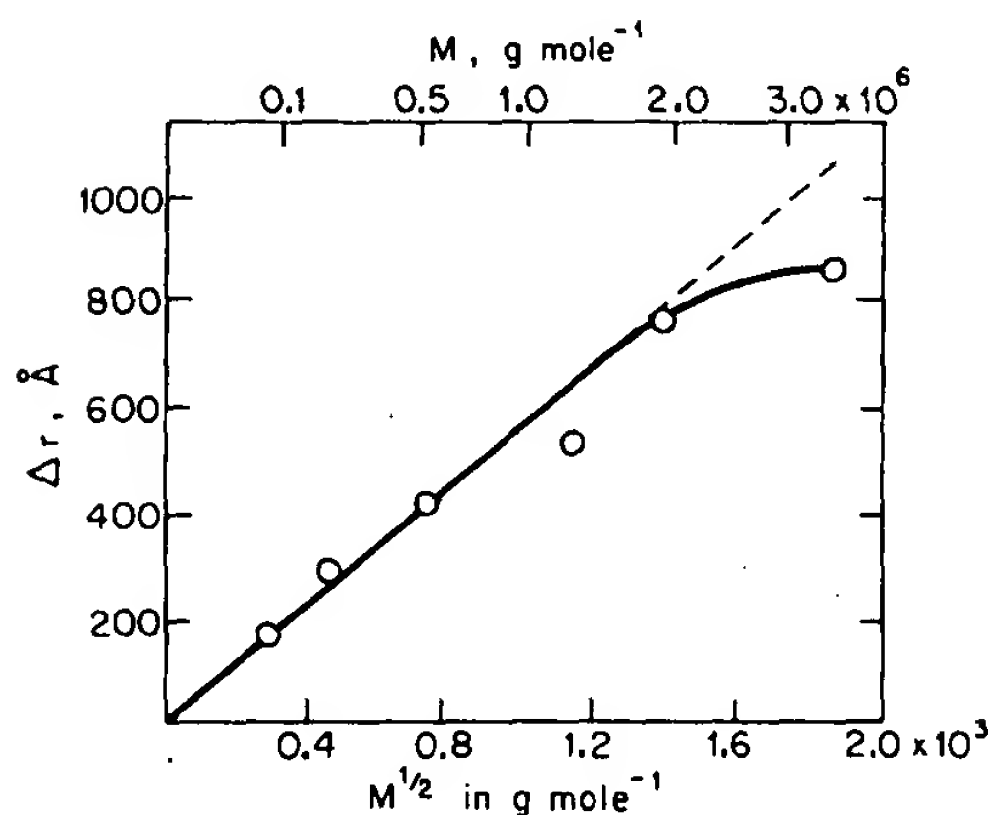


Fig. XI-5. Root-mean-square thickness in the plateau region of polystyrene adsorbed on chrome ferrotyp plate plotted against the square root of the molecular weight. The solvent is cyclohexane. (From Ref. 46.)

expectation, Eq. XI-19, should apparently fail has not been easy. One expectation that is met, however, is that illustrated in Fig. XI-5. The root-mean-square limiting thickness of adsorbed polymer films does tend to increase with the square root of the polymer length, indicating that long segments of polymer do extend into the solution and are coiled much like dissolved polymer is (see also Ref. 62a).

Another deviant aspect of polymer adsorption is that adsorption may *increase* with increasing temperature; the adsorption must then be entropy rather than energy favored. Since the polymer must surely lose entropy on adsorption, the effect must come from a gain in solvent entropy. Yet this gain apparently is not so simply explained as in terms of release of adsorbed solvent to the solution, in view of the failure of Eq. XI-19. The interfacial phase point of view is probably more realistic; adsorbed polymer films can be quite thick, as illustrated in Fig. XI-5. Film thicknesses, Δr in Fig. XI-5, are often measured hydrodynamically, in terms of the increase in the apparent adsorbent particle radius as given by viscosity-concentration measurements. Alternatively, the change in effective pore diameter in capillary flow, following adsorption, may be measured. Ellipsometry has also been used (64, 65).

A complication is that polymer adsorption may be *irreversible*. This aspect is discussed below.

Much attention has been paid to biological polymers such as proteins. See Refs. 66 and 67. Baier (68) has discussed the adsorption of microorganisms. Adsorption of polymer mixtures has been studied, as in Ref. 69.

3. Irreversible Adsorption

There are numerous references in the literature to irreversibility of adsorption from solution, although the phenomenon has not very often been studied explicitly.

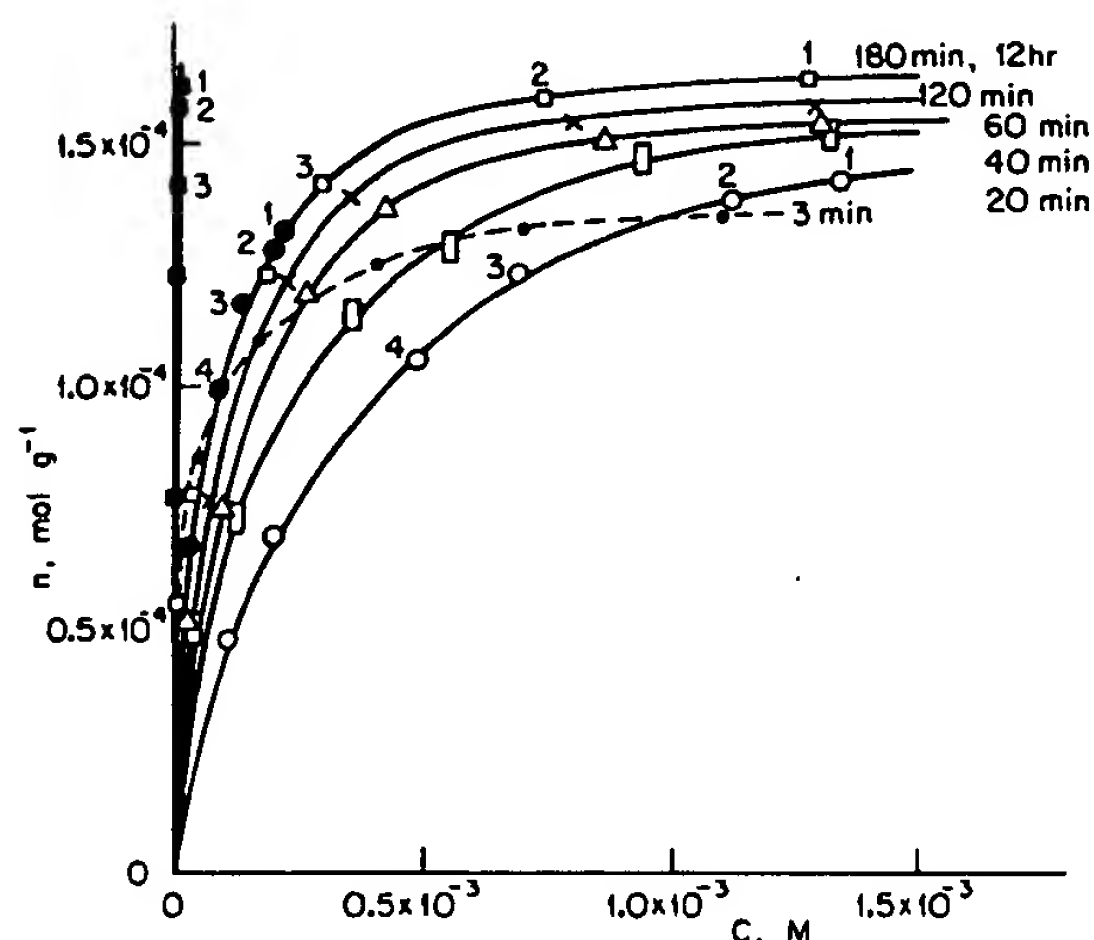


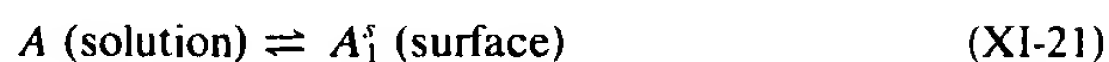
Fig. XI-6. Adsorption of BaDNNS on TiO_2 at 23°C from n -heptane solution. \square , \times , Δ , \square , \circ , \bullet : Adsorption points for the indicated times of equilibration. \blacksquare , \bullet : Desorption points following 12-hr and 20-min equilibrations, respectively. Matching adsorption and desorption points are correspondingly numbered. Reprinted with permission from M. E. Zawadski, Y. Harel, and A. W. Adamson, *Langmuir*, **3**, 363 (1987). (Ref. 81.) Copyright 1987, American Chemical Society.

In the typical experiment, solid adsorbent is equilibrated with solution, and the amount adsorbed is calculated from the drop in the solution concentration of the adsorbate. The behavior that defines *irreversible adsorption* as the term is used here is that if the supernatant solution is removed and the adsorbent equilibrated with the pure solvent, then little or no *desorption* occurs. Typically, there is no evidence of strong adsorbent–adsorbate bond formation, either in terms of the chemistry of the system or from direct calorimetric measurements of the heat of adsorption. It is also typical that if a better solvent is used, or a strongly competitive adsorbate, then desorption is rapid and complete.

Irreversible adsorption has most often been reported in the case of polymer adsorption (70). Stuart and co-workers suggested that the effect is essentially artifactual, being due to polymer polydispersity (71); it is still observed, however, with monodisperse natural and synthetic polymers (72–74). Irreversible adsorption has also been reported for surfactant adsorption on clays and on sandstone (75–78) as well as on metal surfaces (79). Figure XI-6 shows results for the surfactant barium dinonylnaphthalene sulfonate (important as an oil additive) adsorbing on TiO_2 (anatase) and illustrates time effects. Adsorption was irreversible for aged systems, but much less so for ones for which the age of the adsorbed material was small. The adsorption of aqueous methylene blue (note Section XI-4) on TiO_2 (anatase) was also irreversible (80).

Adsorption irreversibility or hysteresis is thus not confined to a single type of adsorbent–adsorbate system, and there may be more than one kind of explanation. It

does seem necessary to postulate at least a two-stage sequence, such as



where A denotes adsorbate, A_1^s is the primarily adsorbed state, which may be in rapid equilibrium with the solution, and A_x^s denotes some kind of polymeric or condensed-phase state (81–84). There remains, however, a fundamental paradox (see Problem 8).

4. Surface Area Determination

The estimation of surface area from solution adsorption studies is subject to many of the same considerations as in the case of gas adsorption, but with the added complication that larger molecules are involved, whose surface orientation and pore penetrability may be uncertain. A first condition is that a definite adsorption model be obeyed, which in practice means that area determinations are limited to cases in which the simple Langmuir equation, Eq. XI-5, holds. The constant n^s is found, for example, from a plot of the data according to Eq. XI-11, and the specific surface area Σ then follows from Eq. XI-6. The problem is to pick the correct value of σ^0 .

In the case of gas adsorption where the BET method is used (Section XVI-5) it is reasonable to use the van der Waals area of the adsorbate molecule; moreover, being small or even monatomic, surface orientation is not a major problem. In the case of adsorption from solution, however, the adsorption may be chemisorption, with σ^0 determined by the spacing of adsorbent sites, or physical adsorption, with σ^0 more determined by the area of the adsorbate molecule in its particular orientation.

Fatty acid adsorption has been used for surface area estimation because of evidence that in many cases the orientation is perpendicular to the surface and with about the close-packed area per molecule of 20.5 \AA^2 . This seems to be true for adsorption on such diverse solids as carbon black and not too electropositive metals, and for TiO_2 . In all of these cases, the adsorption is probably chemisorption in type, involving hydrogen bonding or actual salt formation with surface hydroxyls. Fairly polar solvents are used to avoid multilayer formation on top of the first layer, but even so, the apparent area obtained may vary with the solvent used. In the case of stearic acid on a graphitized carbon surface, Graphon, the adsorption, while still obeying the Langmuir equation, appears to be physical, with the molecules lying flat on the surface. In brief, the method must be applied with caution and with confirmatory evidence.

A second class of adsorbates of which much use has been made is that of dye-stuffs; the method is appealing because of the ease with which analysis may be made colorimetrically. The adsorption generally follows the Langmuir equation but can be multilayer. Graham found an apparent molecular area of 197 \AA^2 for methylene blue on Graphon (85) or larger than the actual molecular area of 175 \AA^2 , but the apparent value for the more oxidized surface of Spheron was about 105 \AA^2 per molecule (86). Some of the problems that may arise, such as due to dye association in solution, are discussed by Padday (87) and Barton (88).

Rahman and Ghosh (89) have used pyridine adsorption on various oxides to obtain surface areas. Adsorption followed the Langmuir equation; the effective molecular area of pyridine is about 24 \AA^2 per molecule.

Two quite different approaches are the following. Everett (90) has proposed a method using binary liquid systems (see the next section); the approach has been discussed more recently by Schay and Nagy (91). Surface areas may be estimated from the exclusion of like charged ions from a charged interface (92). The method, discussed further in Section XI-6, is intriguing in that no estimation of either site or molecular area is called for.

Another kind of problem is that powdered adsorbents are likely to be *fractal* in nature (see Section VII-4C), so that the apparent surface area depends on the size of adsorbate molecule used (see Ref. 93).

5. Adsorption in Binary Liquid Systems

A. Adsorption at the Solid-Solution Interface

The discussion so far has been confined to systems in which the solute species are dilute, so that adsorption was not accompanied by any significant change in the activity of the solvent. In the case of adsorption from binary liquid mixtures, where the complete range of concentration, from pure liquid A to pure liquid B, is available, a more elaborate analysis is needed. The terms solute and solvent are no longer meaningful, but it is nonetheless convenient to cast the equations around one of the components, arbitrarily designated here as component 2.

Adsorption is still defined by Eq. XI-1 but only in the form

$$n_2^s (\text{apparent}) = n_0 \Delta N_2^l \quad (\text{XI-23})$$

since in concentrated solutions, concentration units become awkward to use because density is now also a function of composition; the superscript *l* will be used where helpful to make it clear that the quantity is for the solution phase. Furthermore, the adsorption defined by Eq. XI-23 is now an apparent adsorption, that is, is no longer the actual moles of the component adsorbed. However, it does turn out that the apparent adsorption is simply related to a surface excess quantity, as shown in the following demonstration.

We suppose that the Gibbs dividing surface (see Section III-5) is located at the surface of the solid (with the implication that the solid itself is not soluble). It follows that the surface excess Γ_2^s , according to this definition, is given by (see Problem 7)

$$\Gamma_2^s = \frac{n^s}{\Sigma} (N_2^s - N_2^l) \quad (\text{XI-24})$$

Here, n^s denotes the total number of moles associated with the adsorbed layer, and N_1^s and N_1^l are the respective mole fractions in that layer and in

solution at equilibrium. As before, it is assumed, for convenience, that mole numbers refer to that amount of system associated with one *gram of adsorbent*. Equation XI-24 may be written

$$\Gamma_2^s = \frac{n^s}{\Sigma} \left(\frac{n_2^s}{n^s} - \frac{n_2^l}{n^l} \right) \quad (\text{XI-25})$$

where n_2^s and n_2^l are the moles of component 2 in the adsorbed layer and in solution. Since $n_2^s + n_2^l = n_2^0$, the total number of moles of component 2 present, and $n^s + n^l = n_0$, the total number of moles in the system, substitution into Eq. XI-25 yields

$$\Gamma_2^s = \frac{n_0}{\Sigma} (N_2^0 - N_2^l) = \frac{n_0 \Delta N_2^l}{\Sigma} \quad (\text{XI-26})$$

where N_2^0 is the mole fraction of component 2 before adsorption.

Another form of Eq. XI-26 may be obtained (from Eq. IX-23 and remembering that $N_1^l + N_2^l = 1$ and $n^s = n_1^s + n_2^s$):

$$\Gamma_2^s = \frac{n_0 \Delta N_2^l}{\Sigma} = \frac{n_2^s N_1^l - n_1^s N_2^l}{\Sigma} \quad (\text{XI-27})$$

It is important to note that the experimentally defined or *apparent adsorption* $n_0 \Delta N_2^l / \Sigma$, while it gives Γ_2^s , does *not* give the amount of component 2 in the adsorbed layer n_2^s . Only in dilute solution where $N_2^l \rightarrow 0$ and $N_1^l \approx 1$ is this true. The adsorption isotherm, Γ_2^s plotted against N_2 , is thus a *composite isotherm* or, as it is sometimes called, the *isotherm of composition change*.

Equation XI-27 shows that Γ_2^s can be viewed as related to the difference between the individual adsorption isotherms of components 1 and 2. Figure XI-7 (94) shows the composite isotherms resulting from various combinations of individual ones. Note in particular Fig. XI-7a, which shows that even in the absence of adsorption of component 1, that of component 2 must go through a maximum (due to the N_1^l factor in Eq. XI-27), and that in all other cases the apparent adsorption of component 2 will be negative in concentrated solution.

Everett and co-workers (95) describe an improved experimental procedure for obtaining Γ_i^s quantities. Some of their data are shown in Fig. XI-8. Note the negative region for n_1^s at the lower temperatures. More recent but similar data were obtained by Phillips and Wightman (96).

An elegant and very interesting approach was that of Kipling and Tester (97), who determined the separate adsorption isotherms for the vapors of benzene and of ethanol on charcoal, that is, the adsorbent was equilibrated with the vapor in equilibrium with a given solution, and from the gain in

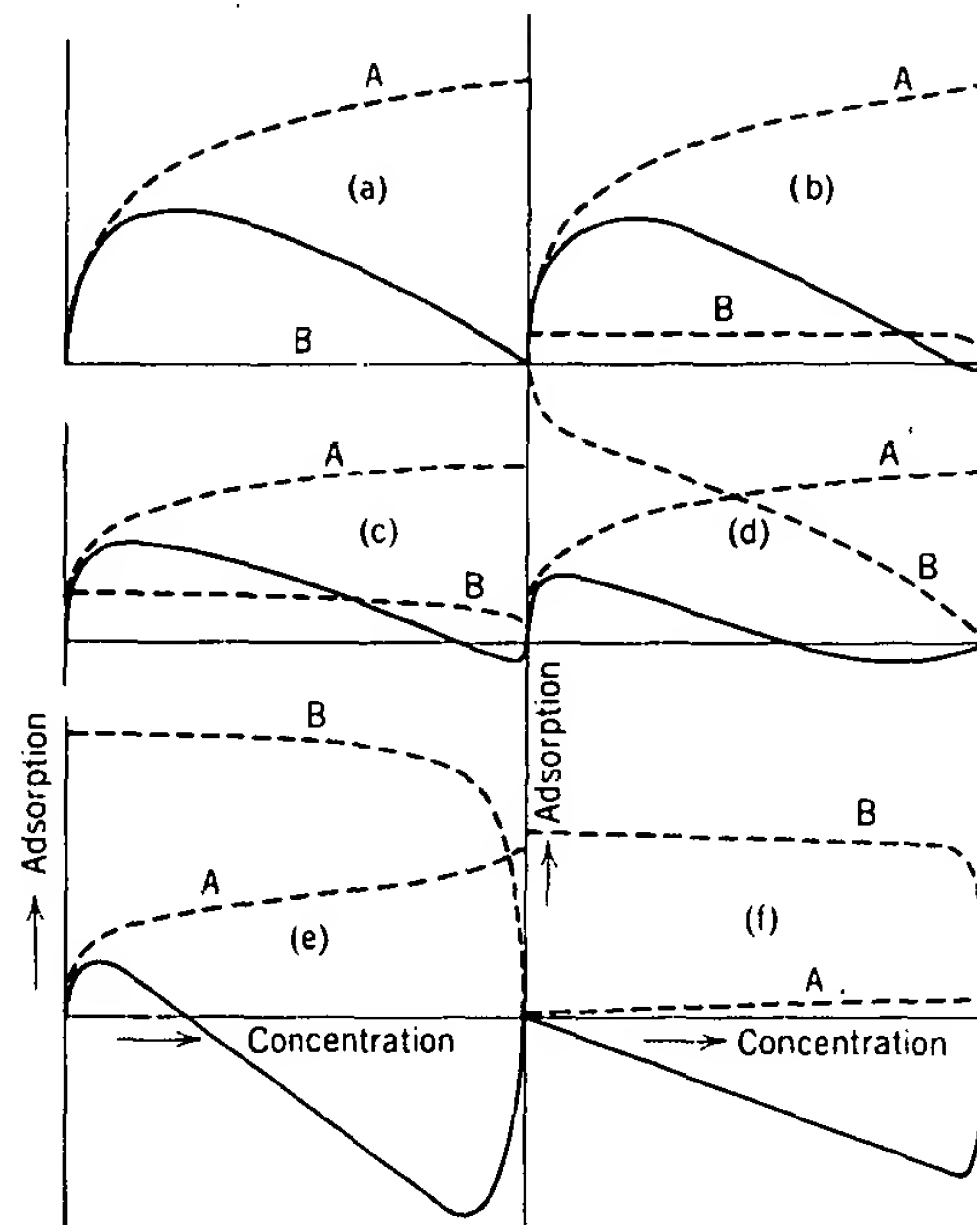


Fig. XI-7. Composite adsorption isotherms; -----, individual isotherms; —, isotherms of composition change. (From Ref. 94.)

weight of the adsorbent and the change in solution composition, following adsorption, the amounts of each component in the adsorbed film could be calculated. These individual component isotherms could then be inserted in Eq. XI-27 to give a calculated apparent solution adsorption isotherm, which in fact agreed well with the one determined directly. Their data are illustrated in Fig. XI-9. They also determined the separate adsorption isotherms for benzene and charcoal and ethanol and charcoal; these obeyed Langmuir equations for gas adsorption,

$$\theta_1 = \frac{b_1 P_1}{1 + b_1 P_1} \quad \theta_2 = \frac{b_2 P_2}{1 + b_2 P_2} \quad (\text{XI-28})$$

from which the constants b_1 and b_2 were thus separately evaluated. The composite vapor adsorption isotherms of Fig. XI-9a were then calculated using these constants and the added assumption that in this case no bare surface was present. The Langmuir equation for the competitive adsorption of two gas phase components is (see Section XVI-3)

$$\theta_2 = \frac{b_2 P_2}{1 + b_1 P_1 + b_2 P_2} \quad (\text{XI-29})$$

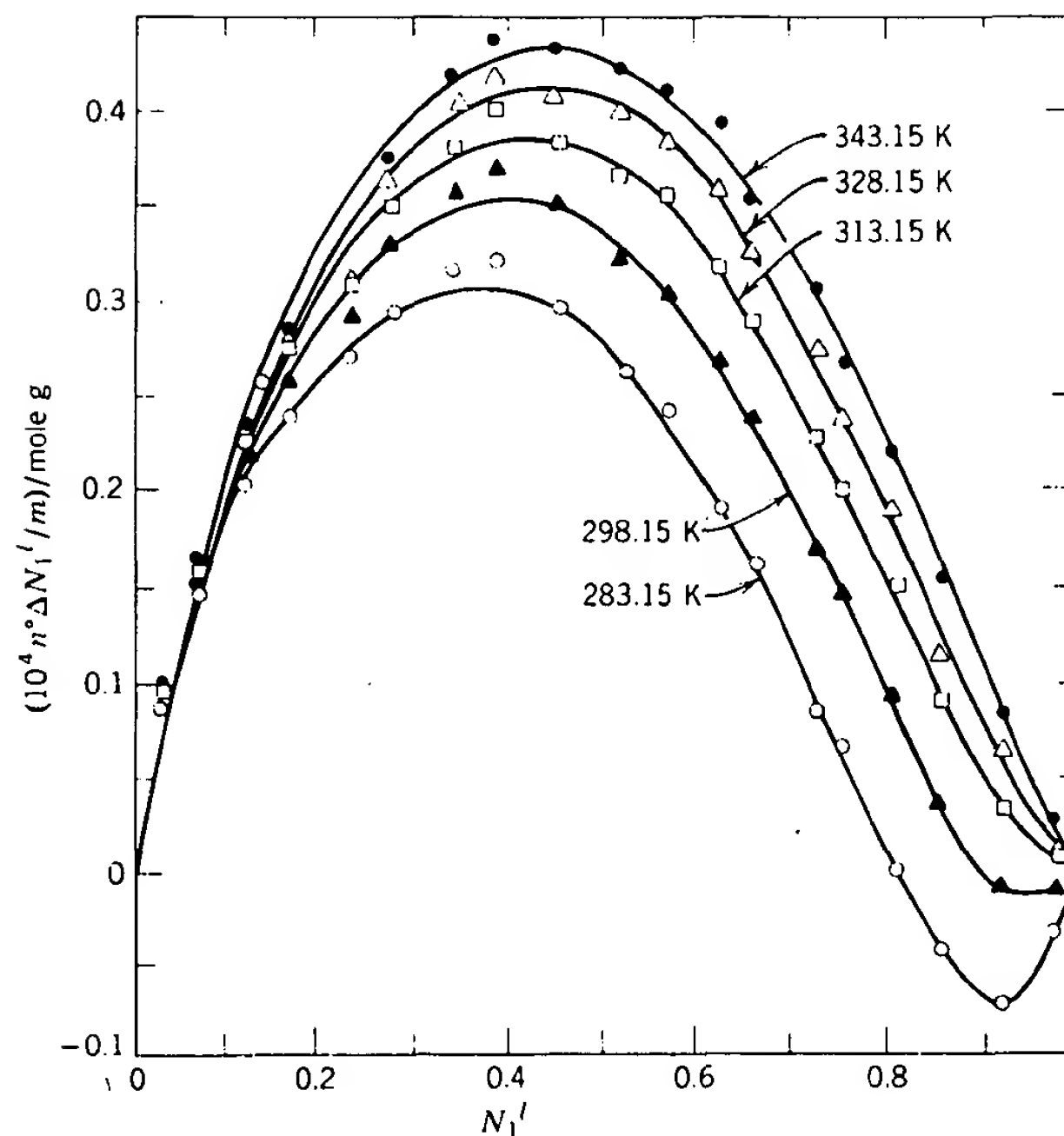


Fig. XI-8. Isotherm of composition change or surface excess isotherm for the adsorption of (1) benzene and (2) *n*-heptane on Graphon. (From Ref. 95.)

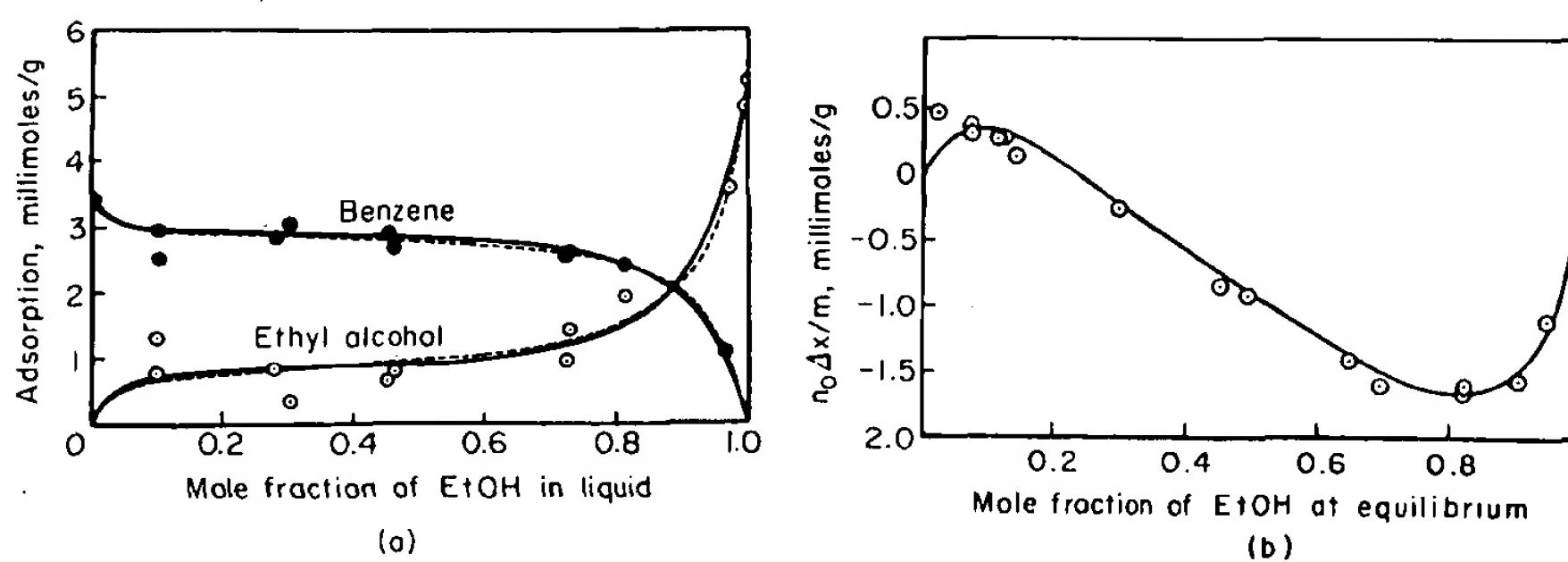


Fig. XI-9. Relation of adsorption from binary liquid mixtures to the separate vapor pressure adsorption isotherms system: ethanol-benzene-charcoal: (a) separate mixed vapor isotherms; (b) calculated and observed adsorption from liquid mixtures. (From Ref. 97.)

and the effect of their assumptions was to put Eq. XI-29 in the form

$$\theta_2 = \frac{b_2 P_2}{b_1 P_1 + b_2 P_2} \approx \frac{b_2 P_2^0 N_2^l}{b_1 P_1^0 N_1^l + b_2 P_2^0 N_2^l} \quad (\text{XI-30})$$

and to identify b_2 and b_1 with the separately determined values from Eqs. XI-28. Again, good agreement was found, as shown by the dashed lines in Fig. XI-9a. Similar comparisons have been made by Myers and Sircar (98).

The Langmuir model as developed in Section XI-1 may be applied directly to Eq. XI-24 (7). We replace a_1 and a_2 in Eq. XI-3 by N_1 and N_2 (omitting the superscript l as no longer necessary for clarity), and solve for N_2^s (with N_1 replaced by $1 - N_2$):

$$N_2^s = N_2 \frac{K}{1 + (K - 1)N_2} \quad (\text{XI-31})$$

This is now substituted into Eq. XI-22, giving

$$\Gamma_2^s = \frac{n^s (K - 1)N_1 N_2}{\Sigma 1 + (K - 1)N_2} \quad (\text{XI-32})$$

Or, using the apparent adsorption, $n^0 \Delta N_2$, Eq. XI-30 may be put in the linear form

$$\frac{N_1 N_2}{n_0 \Delta N_2} = \frac{1}{n^s (K - 1)} + \frac{1}{n^s} N_2 \quad (\text{XI-33})$$

which bears a close resemblance to that for the simple Langmuir equation, Eq. XI-4. Note that for $K = 1$, $\Gamma_2^s = 0$, that is, no fractionation occurs at the interface. Everett (7) found Eq. XI-33 to be obeyed by several systems, for example, that of benzene and cyclohexane on Spheron 6.

In general, one should allow for nonideality in the adsorbed phase (as well as in solution), and various authors have developed this topic (7, 92, 99, 100–102). Also, the adsorbent surface may be heterogeneous, and Sircar (103) has pointed out that a given set of data may equally well be represented by nonideality of the adsorbed layer on a uniform surface or by an ideal adsorbed layer on a heterogeneous surface.

Isotherms of type a in Fig. XI-7 are relatively linear for large N_2 , that is,

$$n_0 \Delta N_2^l = a - b N_2^l \quad (\text{XI-34})$$

Now, Eq. XI-27 can be written in the form

$$n_0 \Delta N_2^l = n_2^s - n^s N_2^l \quad (\text{XI-35})$$

(since $n^s = n_1^s + n_2^s$ and $N_1 + N_2 = 1$). Comparing Eqs. XI-34 and XI-35, the slope b gives the monolayer capacity n^s . The surface area Σ follows if the molecular area can be estimated. The treatment assumes that in the linear region the surface is mostly occupied by species 2 so that n_2^s is nearly constant. See Refs. 104 and 105.

There is a number of very pleasing and instructive relationships between adsorption from a binary solution at the solid-solution interface and that at the solution-vapor and the solid-vapor interfaces. The subject is sufficiently specialized, however, that the reader is referred to the general references and, in particular, to Ref. 31. Finally, some studies on the effect of high pressure (up to several thousand atmospheres) on binary adsorption isotherms has been reported (106). Quite appreciable effects were found, indicating that significant partial molal volume changes may occur on adsorption.

B. Heat of Adsorption at the Solid-Solution Interface

Rather little has been done on heats of wetting of a solid by a solution, but two examples suggest a fairly ideal type of behavior. Young et al. (100) studied the Graphon-aqueous butanol system, for which monolayer adsorption of butanol was completed at a fairly low concentration. From direct adsorption studies, they determined θ_b , the fraction of surface covered by butanol, as a function of concentration. They then prorated the heat of immersion of Graphon in butanol, 113 ergs/cm², and of Graphon in water, 32 ergs/cm², according to θ_b . That is, each component in the adsorbed film was considered to interact with its portion of the surface independently of the other,

$$q_{\text{imm}} = N_1^s q_1 + N_2^s q_2 \quad (\text{XI-36})$$

where q_{imm} is the heat of immersion in the solution and q_1 and q_2 are the heats of immersion in the respective pure liquid components. To this prorated q_{imm} was added the heat effect due to concentrating butanol from its aqueous solution to the composition of the interfacial solution using bulk heat of solution data. They found that their heats of immersion calculated in this way agreed very well with the experimental values.

As a quite different and more fundamental approach, the isotherms of Fig. XI-8 allowed a calculation of K as a function of temperature. The plot of $\ln K$ versus $1/T$ gave an enthalpy quantity which should be just the difference between the heats of immersion of the Graphon in benzene and in *n*-heptane, or 2.6×10^{-3} cal/m² (95). The experimental heat of immersion difference is 2.4×10^{-3} cal/m², or probably indistinguishable. The relationship between calorimetric and isosteric heats of adsorption has been examined further by Myers and Sircar (107).

6. Adsorption of Electrolytes

The interaction of an electrolyte with an adsorbent may take one of several forms. Several of these are discussed, albeit briefly, in what follows.

The electrolyte may be adsorbed *in toto*, in which case the situation is similar to that for molecular adsorption. It is more often true, however, that ions of one sign are held more strongly, with those of the opposite sign forming a diffuse or secondary layer. The surface may be polar, with a potential ψ , so that primary adsorption can be treated in terms of the Stern model (Section V-4), or the adsorption of interest may involve exchange of ions in the diffuse layer.

In the case of ion exchangers, the primary ions are chemically bonded into the framework of the polymer, and the exchange is between ions in the secondary layer. A few illustrations of these various types of processes follow.

A. Stern Layer Adsorption

Adsorption at a charged surface where both electrostatic and specific chemical forces are involved has been discussed to some extent in connection with various other topics. These examples are drawn together here for a brief review along with some more specific additional material. The Stern equation, Eq. V-25, may be put in a form more analogous to the Langmuir equation, Eq. XI-5:

$$\frac{\theta}{1 - \theta} = C_2 \exp \frac{ze\psi + \phi}{kT} \quad (\text{XI-37})$$

The effect is to write the adsorption free energy or, approximately, the energy of adsorption Q as a sum of electrostatic and chemical contributions. A review is provided by Ref. 107a.

Stern layer adsorption was involved in the discussion of the effect of ions on ζ potentials (Section V-8), electrocapillary behavior (Section V-9), and electrode potentials (Section V-10) and enters into the effect of electrolytes on charged monolayers (Section IV-13). More specifically, this type of behavior occurs in the adsorption of electrolytes by ionic crystals. A large amount of work of this type has been done, partly because of the importance of such effects on the purity of precipitates of analytical interest and partly because of the role of such adsorption in coagulation and other colloid chemical processes. Early studies include those by Weiser (108), by Paneth, Hahn, and Fajans (109), and by Kolthoff and co-workers (110).

It is possible for neutral species to be adsorbed even where specific chemical interaction is not important owing to a consequence of an electrical double layer. As discussed in connection with Fig. V-4, the osmotic pressure of solvent is reduced in the region between two charged plates. There is, therefore, an equilibrium with bulk solution that can be shifted by changing the external ionic strength. As a typical example of such an effect, the interlayer spacing of montmorillonite (a sheet or layer type alumino-silicate see Fig. XI-10) is very dependent on the external ionic strength. A spacing of

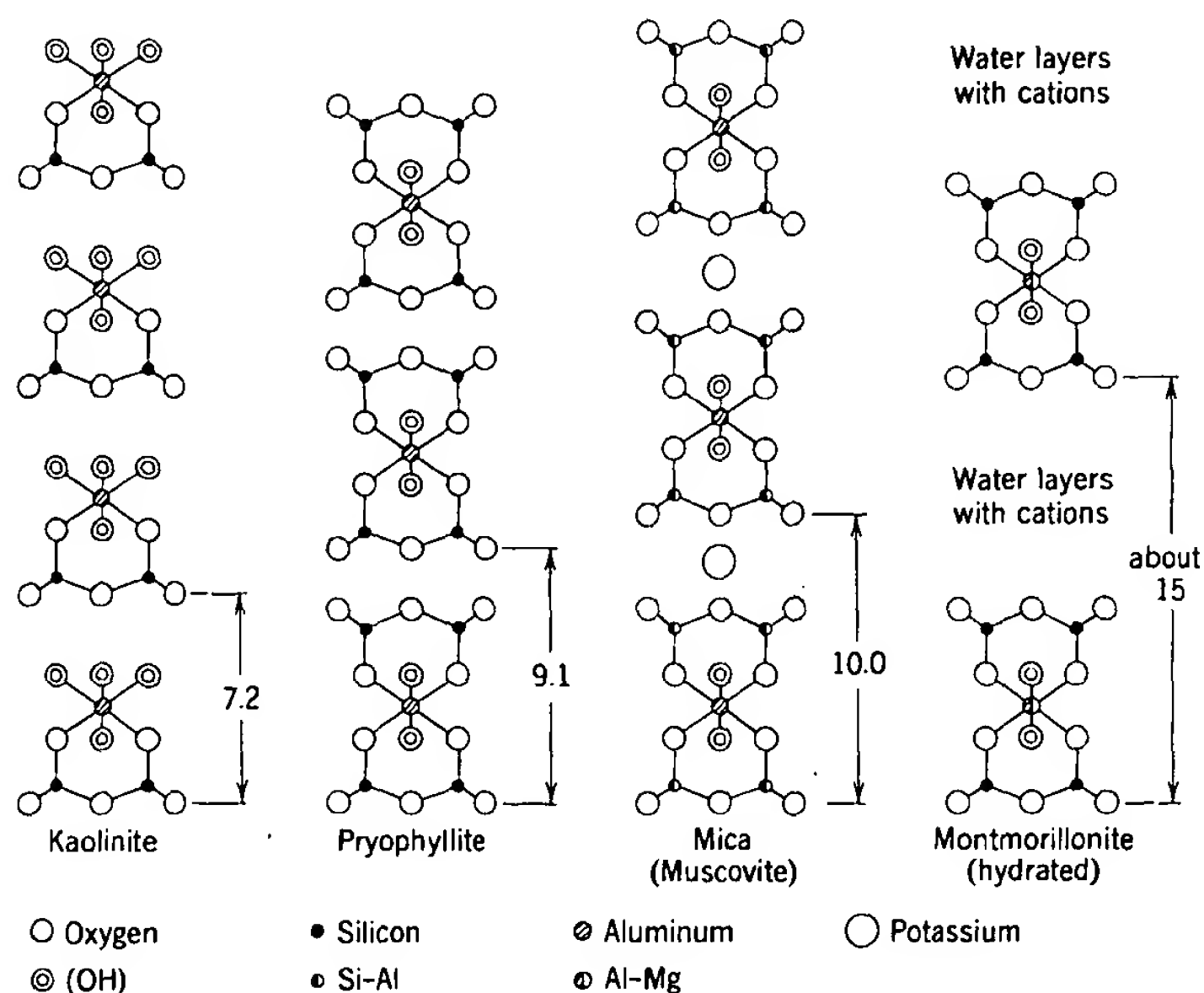


Fig. XI-10. End-on view of the layer structures of clays, pyrophyllite, and mica. (From Ref. 112.)

about 19 Å in dilute electrolyte reduces to about 15 Å in 1–2 M 1:1 electrolyte (111). Phenomenologically, a strong water adsorption is repressed by added electrolyte.

If specific chemical interactions are not dominant, the adsorption of an ionic species is largely determined by its charge. This is the basis for an early conclusion by Bancroft (113) that the order of increasing adsorption of ions by sols is that of increasing charge. Within a given charge type, the sequence may be that of increasing hydration enthalpy (114); thus: $\text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+$, $\text{K}^+ > \text{Ag}^+ > \text{Na}^+ > \text{Li}^+$. The extent of adsorption in turn determines the power of such ions to coagulate sols and accounts for the related statement that the coagulating ability of an ion will be greater the higher its charge. This rule, the Schulze–Hardy rule, is discussed in Section VI-5B.

Very often both chemical and electrical interactions are important. For example, Connor and Ottewill concluded that the adsorption of long-chain quaternary ammonium ions on latex particles was at first largely electrostatic (115). The surface initially is negatively charged, owing to surface carboxyl groups. At the knee of the isotherm shown in Fig. XI-11, this surface charge has been neutralized (the direction of electrophoretic motion of the particles reverses), and the further adsorption is due to attraction of the alkyl chains to the surface. At the highest concentrations some association may be occurring. Fuerstenau and co-workers have in fact proposed

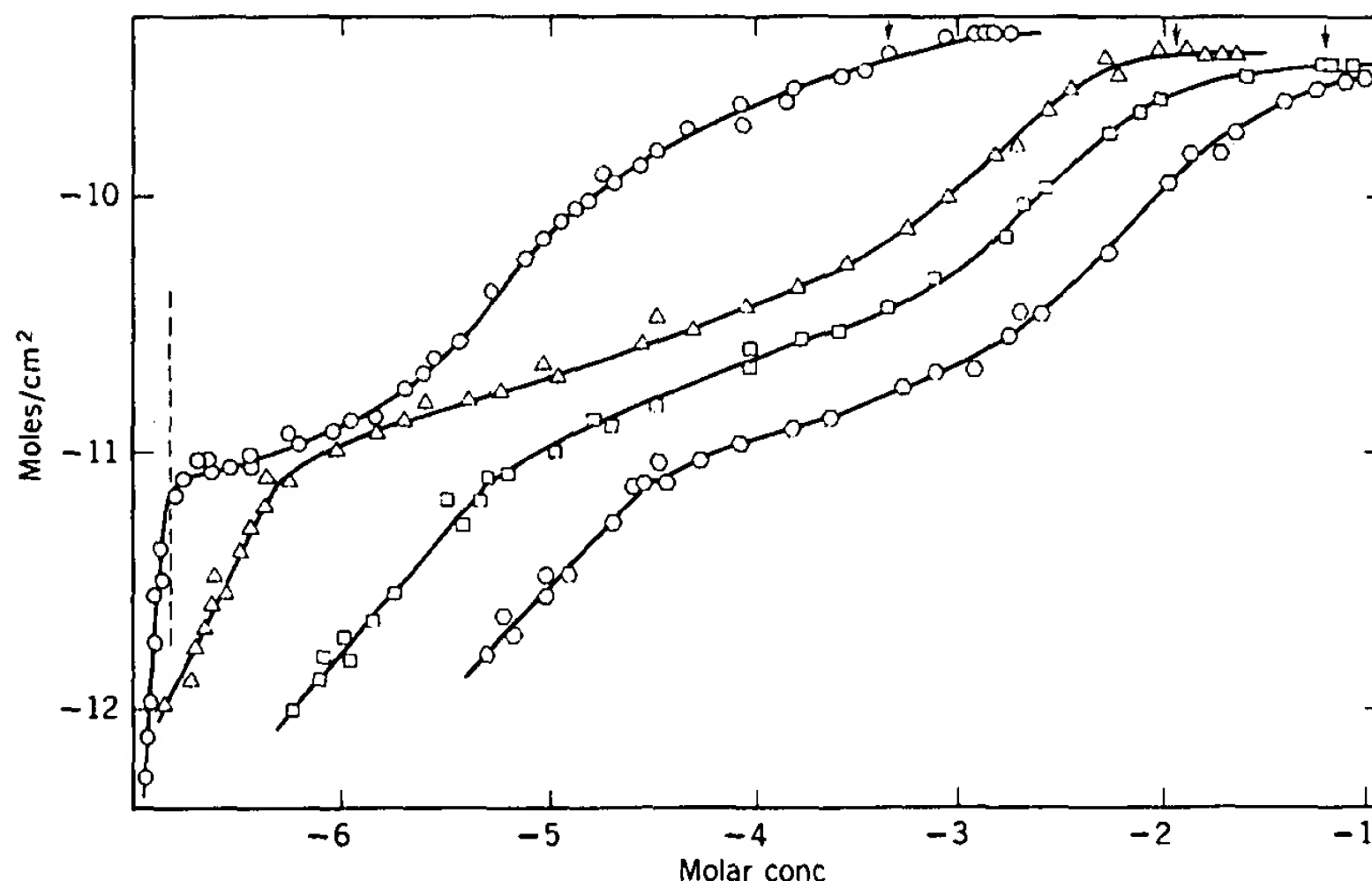


Fig. XI-11. Adsorption isotherms on particles of Latex-G at pH 8 in $10^{-3} M$ KBr solution: \circ , hexadecyltrimethylammonium ion; Δ , dodecyltrimethylammonium ion; \square , decyltrimethylammonium ion; \diamond , octyltrimethylammonium ion. Arrows mark the cmc values; the vertical dashed line marks the reversal of charge for the hexadecyltrimethylammonium ion case. (From Ref. 115).

that in systems of this kind (a specific one for them being that of sodium dodecylbenzene sulfonate on alumina) a surface aggregation occurs to give *hemimicelles* (116). The allusion is to the micelles that colloidal electrolytes form in solution above a certain concentration—the critical micelle concentration (cmc) (see Section XIII-5). While it is reasonable to suppose that surface association can occur, it is questionable whether the structure could be like that of solution micelles.

The effect of adsorption on the charge of the adsorbent particles may be determined from electrophoretic measurements and then expressed as changes in ζ potential. An example is provided by Fig. XI-12, showing that adsorption of cations by quartz eventually reduces the ζ to zero. If, much in the manner of Traube's rule studies (Section XI-1B), the concentration required to give zero ζ potential is regarded as determined primarily by ϕ in Eq. XI-37, then the observation that $\log C_2$ showed a linear dependence of chain length can be accounted for. Moreover, the slope $(\partial \ln C_2 / \partial n)_{\zeta=0}$, where n is the chain length, gave an energy increment of about 600 cal/ CH_2 group, or about the same as at the water-air interface (see Section III-7E). Fuerstenau interprets this as evidence for surface association or "hemimicelle" formation. See Ref. 117a for illustration of chain length effects in the case of alkylbenzene sulfonates adsorbed on mineral oxides.

Surface charge may be controlled or fixed by a potential-determining ion.

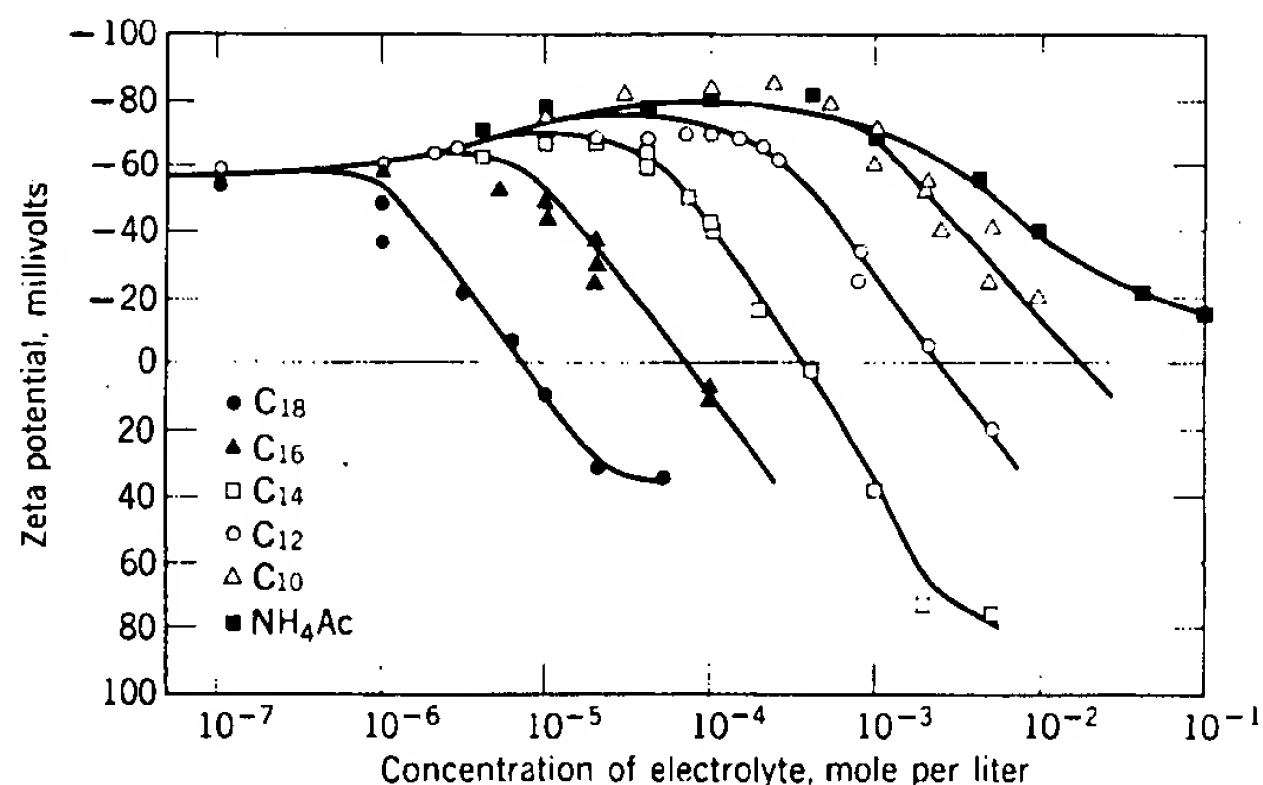


Fig. XI-12. Effect of hydrocarbon chain length on the ζ potential of quartz in solutions of alkylammonium acetates and in solutions of ammonium acetate. (From Ref. 117.)

Table XI-1 (from Ref. 118) lists the potential-determining ion and its concentration giving zero charge on the mineral. There is a large family of minerals for which hydrogen (or hydroxide) ion is potential determining—oxides, silicates, phosphates, carbonates, and so on. For these, adsorption of surfactant ions is highly pH dependent. An example is shown in Fig. XI-13. This type of behavior has important applications in flotation and is discussed further in Section XIII-4C.

Electrolyte adsorption on metals is important in electrochemistry. One study reports the adsorption of various anions on Ag, Au, Rh, and Ni electrodes using ellipsometry. Adsorbed film thicknesses now also depend on applied potential (see Refs. 119, 120).

TABLE XI-1
Potential-determining Ion and Point of Zero Charge^a

Material	Potential-determining Ion	Point of Zero Charge
Fluorapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH})$	H^+	pH 6
Hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	H^+	pH 7
Alumina, Al_2O_3	H^+	pH 9
Calcite, CaCO_3	H^+	pH 9.5
Fluorite, CaF_2	Ca^{2+}	pCa 3
Barite (synthetic), BaSO_4	Ba^{2+}	pBa 6.7
Silver iodide	Ag^+	pAg 5.6
Silver chloride	Ag^+	pAg 4
Silver sulfide	Ag^+	pAg 10.2

^a From Ref. 118.

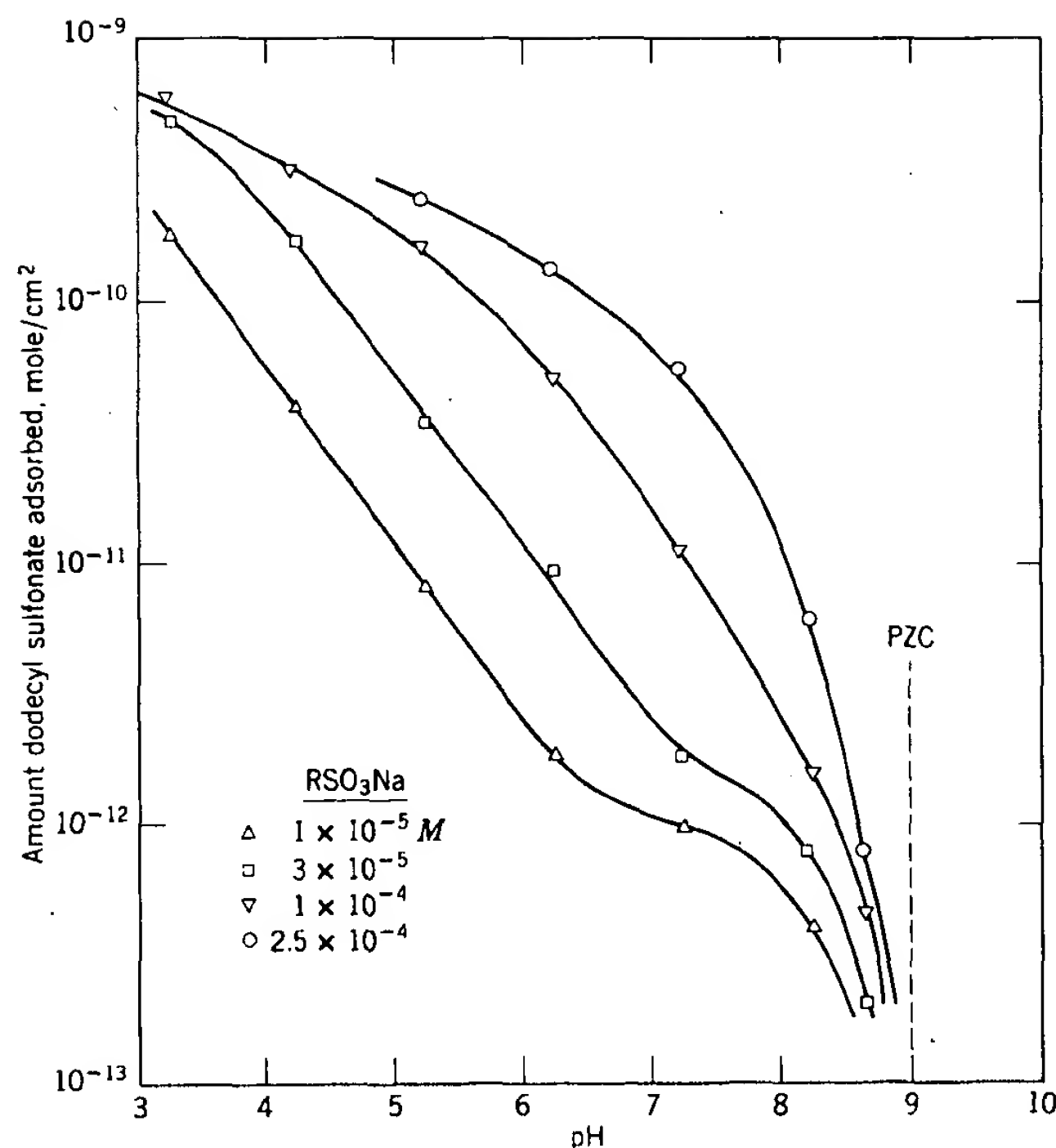


Fig. XI-13. Adsorption of sodium dodecyl sulfonate on alumina as a function of pH in $2 \times 10^{-3} M$ NaCl solution. (From Ref. 118.)

B. Surface Areas from Negative Adsorption

An interesting application of electrical double-layer theory has been to the estimation of surface area from the degree of *exclusion* from the solid-solution interface of ions having the same charge as that at the interface. According to Eq. V-2 and as illustrated in Fig. V-1, the concentration of negative ions should diminish near a negatively charged interface. As a consequence of this exclusion, the solution concentration should increase from n_0 to n'_0 on equilibration with the solid. By material balance,

$$\mathcal{A}\Gamma^- = V \Delta n_0 \quad (\text{XI-38})$$

where \mathcal{A} is the surface area of solid added to volume V of solution, Γ^- is the surface (negative) adsorption of the negative ions, and $\Delta n_0 = n'_0 - n_0$ is the increase in concentration.

Referring to Fig. V-1, the negative adsorption is given by

$$\Gamma^- = \int_0^\infty (n'_0 - n^-) dx \quad (\text{XI-39})$$

A final expression results if n^- is replaced by the appropriate Eq. V-2, and dx expressed in terms of $d\psi$ by means of Eq. V-11. In simplifying the result, Van den Hul and Lyklema (92) obtain the approximate equation for aqueous 1:1 electrolyte solutions at 20°C:

$$\mathcal{A} = \frac{0.52 \times 10^9 V \Delta n_0}{\sqrt{n_0'}} \quad (\text{XI-40})$$

where V is in cubic centimeters and concentrations are in moles per cubic centimeter. The method was applied successfully to the measurement of the surface area of AgI suspensions; the required assumption that ψ_0 was constant (and high) was met by addition of suitable concentration of I^- ions. See Schofield (121, 122) and Edwards and Quirk (123) for additional examples.

C. Counterion Adsorption—Ion Exchange

A very important class of adsorbents consists of those having charged sites due to ions or ionic groups bound into the lattice. The montmorillonite clays, for example, consist of layers of tetrahedral SiO_4 units sharing corners with octahedral Al^{3+} , having coordinated oxygen and hydroxyl groups, as illustrated in Fig. XI-10 (112). In not too acid solution, cation exchange with protons is possible, and because of the layer structure, swelling effects occur, which are understandable in terms of ionic strength effects on double-layer repulsion (see Section VI-6B and Ref. 124).

The aluminum silicate can be regarded as networks of silicate tetrahedra with some replacement by aluminum, so that electroneutrality requires the inclusion of hydroxyl groups (i.e., protons) or of other cations. A tremendous variety of structures is known, and some of the three-dimensional network ones are porous enough to show the same type of swelling phenomena as the layer structures—and also ion exchange behavior. The zeolites fall in this last category and have been studied extensively, both as ion exchangers and as gas adsorbents (e.g., Refs. 125 and 126). As a recent example, Goulding and Talibudeen have reported on isotherms and calorimetric heats of Ca^{2+} – K^+ exchange for several aluminosilicates (127).

Organic ion exchangers were introduced in 1935, and a great variety is now available. The first ones consisted of phenol–formaldehyde polymers into which natural phenols had been incorporated, but now various polystyrene polymers are much more common. Here RSO_3^- groups, inserted by sulfonation of the polymer, are sufficiently acidic that ion exchange can occur even in quite acid solution. The properties can be controlled by varying the degree of sulfonation and of cross-linking. Other anionic groups, such as RCOO^- , may be introduced to vary the selectivity. Also, anion exchangers having RNH_2 groups are in wide use. Here addition of acid gives the $\text{RNH}_3^+ \text{X}^-$ function, and anions may now exchange with X^- .

Both the kinetics and the equilibrium aspects of ion exchange involve more than purely surface chemical considerations. Thus, the formal expres-

sion for the exchange,



where R denotes the matrix and A and B the exchanging ions, suggests a simple mass action treatment. The AR and BR centers are distributed throughout the interior of the exchanger phase and can be viewed as forming a nonideal solution. One may represent their concentrations in terms of mole fractions or, for ions of differing charge, equivalent fractions (this point is discussed in Ref. 128); sizable activity coefficient corrections are generally needed. Alternatively, the exchanger phase may be treated as essentially a concentrated electrolyte solution so that volume concentrations are used, but again with activity coefficient corrections. The nonideality may be approached by considering the exchanger phase to act as a medium permeable to cations but not to the R or lattice ions, so that ion exchange appears as a Donnan equilibrium (see Section IV-10B), and specific recognition can then be given to the swelling effects that occur. Finally, detailed surface structural information may be obtained from surface spectroscopic techniques, as in ESCA (Section VIII-4B) of ion exchange on cleaved mica surfaces (129).

The rates of ion exchange are generally determined by diffusion processes; the rate-determining step may either be that of diffusion across a boundary film of solution or that of diffusion in and through the exchanger base (130). The whole matter is complicated by electroneutrality restrictions governing the flows of the various ions (131, 132).

As may be gathered, the field of ion exchange adsorption and chromatography is far too large to be treated here in more than this summary fashion. Refs. 133 and 134 are useful monographs.

7. Photophysics and Photochemistry of the Adsorbed State

There is a large volume of contemporary literature dealing with the structure and chemical properties of species adsorbed at the solid-solution interface, making use of various spectroscopic and laser excitation techniques. Much of it is phenomenologically oriented and does not contribute in any clear way to the surface chemistry of the system; included are many studies aimed at the eventual achievement of solar energy conversion. What follows here is a summary of a small fraction of this literature, consisting of references which are representative and which also yield some specific information about the adsorbed state.

A. Photophysics of Adsorbed Species

The typical study consists of adsorbing a species having a known photoexcited emission behavior and observing the emission spectrum, lifetime, and quenching by either coadsorbed or solution species. Pyrene and surfactants containing a pyrene

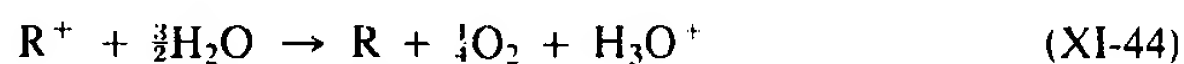
moiety have been widely used, and also the complex ion $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$. R. Pyrene, P, has the property of *excimer* formation, that is, formation of the complex PP^* , where P^* denotes excited-state pyrene, and the emission from PP^* can give information about surface mobility. Both pyrene emission and that from R^* have spectral and lifetime characteristics that are sensitive to local environment. Emission from R^* may be quenched by electron-accepting or electron-donating species; in fact, it is the powerful oxidizing and reducing nature of R^* that has made it an attractive candidate for solar energy conversion schemes.

Surface heterogeneity may be inferred from emission studies, as in studies by de Schryver and co-workers on P and on R adsorbed on clay minerals (135, 136). In the case of adsorbed pyrene and its derivatives, there is considerable evidence for surface mobility (on clays, metal oxides, sulfides), as from the work of Thomas (137), de Mayo and Ware and co-workers (138), and Singer (139); there has also been evidence for ground-state bimolecular association of adsorbed pyrene (140). Pyrene or other emitters may be used as a probe to study the structure of an adsorbate film, as in the case of Triton X-100 adsorbed at the aqueous silica interface (141) and sodium dodecyl sulfate at the aqueous alumina interface (142). In both cases progressive structural changes were concluded to occur with increasing surfactant adsorption. In the case of $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ adsorbed on porous Vycor glass, it was inferred that structural perturbation occurs in the excited state, R^* , but not in the ground state (142a).

Many of the adsorbents used have "rough" surfaces; they may consist of clusters of very small particles, for example. It appears that the concept of self-similarity or fractal geometry (see Section VII-4C) may be applicable (143, 144). In the case of quenching of emission by a coadsorbed species, Q , some fraction of Q may be "hidden" from the emitter if Q is a small molecule that can fit into surface regions not accessible to the emitter (144).

B. Photochemistry at the Solid-Solution Interface

The most abundant literature is that bearing on solar energy conversion, mainly centered on the use of $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ and its analogues. The excited state of the parent compound was found some years ago to be a powerful reducing agent (145), allowing the following spontaneous reactions to be written:



It is thus energetically feasible for R to catalyze the use of visible light to "split" water. The problem is that the reactions are multielectron ones and the actual individual steps are highly subject to reversal or to interception, leading to unproductive degradation of the excitation energy. Much use has been made of heterogeneous systems in an effort to avoid the problem. Thus, if R is adsorbed on a semiconductor such as TiO_2 , R^* might inject an electron into the conduction band of the adsorbent.

which might then migrate away and thus not back-react with the R^+ formed. The subject has been extensively reviewed (see Refs. 146, 147), along with the general photophysical behavior of TiO_2 (148).

Silica and silicates have been used as a support for $Ru(II)$ complexes (149–152), as has porous Vicor glass (153) and clays (154). Photoproduction of hydrogen using Pt-doped TiO_2 has been reported (155), as well as the photodecomposition of water using Pd and Ru doping (156). Iron oxide ($\alpha-Fe_2O_3$) is also effective (157), as is a mixture of supported CdS and Pt on oxide particles (158). CdS, again a semiconductor (159), promotes both photoisomerization (160) and electron transfer (161). Other surface photochemistries include that of ketones on various silicas (162) and zeolites (163), enone cycloaddition on silica gel (164), and surface-bound carbonyl complexes of $Ru(0)$ (165). $Ru(2,2'$ -bipyridine) $_3^{2+}$ promotes the photoreduction of anthraquinones (on SiO_2 and ZrO_2) (166) and the hydrogenation of ethylene and acetylene (using colloidal Pt and Pd) (167), and Ru complexes can promote the photocleavage of C_2H_2 to give CH_4 (168).

Returning to the matter of water splitting, no commercially attractive system has been found—yields are too low, UV light is needed, and a sacrificial reagent is used whose cost is prohibitive. A great deal of interesting surface chemistry and photo-physics has been learned in the process, however. Actually, reaction XI-45 is of dubious practicality even if it were feasible since an explosive and difficultly separable mixture of gases is produced. Of much greater potential value would be the photoreduction of CO_2 to CH_4 (by water), and this reaction has actually been reported to occur using a Ru colloid and a $Ru(II)$ complex (169).

8. Problems

1. An adsorbed film obeys a modified Amagat equation of state, $\pi\sigma = qkT$ (see Eq. III-107). Show that this corresponds to a Freundlich adsorption isotherm (Eq. XI-15) and comment on the situation.

2. One hundred milliliters of an aqueous solution of methylene blue contains 3.0 mg dye per liter and has an optical density (or molar absorbency) of 0.80 at a certain wavelength. The solution is then equilibrated with 25 mg of a charcoal, and the supernatant solution is now found to have an optical density of 0.20. Estimate the specific surface area of the charcoal.

3. The adsorption of stearic acid from *n*-hexane solution on a sample of steel powder is measured with the following results:

Concentration (mM/li)	Adsorption (mg/g)	Concentration (mM/li)	Adsorption (mg/g)
0.01	0.786	0.15	1.47
0.02	0.864	0.20	1.60
0.04	1.00	0.25	1.70
0.07	1.17	0.30	1.78
0.10	1.30	0.50	1.99

Explain the behavior of this system, and calculate the specific surface area of the steel.

4. Dye adsorption from solution may be used to estimate the surface area of a powdered solid. Suppose that if 2.0 g of a bone charcoal is equilibrated with 100 cm³ of initially $10^{-4} M$ methylene blue, the final dye concentration is $0.4 \times 10^{-4} M$, while if 4.0 g of bone charcoal had been used, the final concentration would have been $0.2 \times 10^{-4} M$.

Assuming that the dye adsorption obeys the Langmuir equation, calculate the specific surface area of the bone charcoal in square meters per gram. The molecular area of methylene blue in a monolayer may be taken to be 65 \AA^2 .

5. The adsorption of Aerosol OT on Vulcan R was found to obey the Langmuir equation (170). The plot of C/x versus C was linear, where C is in millimoles per liter and x is in micromoles per gram. For $C = 0.5$, C/x was 100; the plot went essentially through the origin. Calculate the saturation adsorption in micromoles per gram.

6. The adsorption of stearic acid on Spheron 6 was measured using various solvents, with the results shown.

Solvent	Millimoles Adsorbed per Gram at:	
	$N_2 = 0.001$	$N_2 = 0.004$
Cyclohexane	0.030	0.050
Ethyl alcohol	0.015	0.025
Benzene	0.008	0.010

Calculate for each case the apparent specific surface area of the Spheron, assuming the Langmuir equation to hold. State any other assumptions made; discuss the significance of your results.

7. Referring to Eq. XI-1, show that $\sum n_i^* = 0$ if the sum is over all of the solution components.

8. Irreversible adsorption as defined in Section XI-3 poses a paradox. Consider, for example, curve 1 of Fig. XI-4 and for a particular system, let the "equilibrium" concentration be 0.025 g/100 cm^3 , with a corresponding θ value of about 0.5. If the adsorption is irreversible, no desorption would occur on a small dilution; on the other hand, more adsorption would occur if the concentration were increased. If adsorption is possible, but not desorption, why does adsorption *stop* at $\theta = 0.5$ instead of continuing up to $\theta = 1$? This is the paradox. Comment on it and on possible explanations.

9. Derive Eq. XI-24.

10. In a study of the effect of pressure on adsorption, for a system obeying the Langmuir equation (and Eq. XI-3 assuming ideal solutions and $a_1 = 1$), the value of K is 3.32×10^4 at 1 atm pressure and 1.31×10^4 at 3000 bar pressure at 25°C . Consult appropriate thermodynamics texts, and calculate ΔV , the volume change for the adsorption process of Eq. XI-2. Comment on the physical significance of ΔV .

11. For the adsorption on Spheron 6 from benzene-cyclohexane solutions, the plot of $N_1 N_2 / n_0 \Delta N_2$ versus N_2 (cyclohexane being component 2) has a slope of 2.3 and an intercept of 0.4. (a) Calculate K . (b) Taking the area per molecule to be 40 \AA^2 , calculate the specific surface area of the Spheron 6. (c) Make a plot of the isotherm of composition change. Note: assume n^s is in millimoles per gram.

12. Equation XI-30,

$$n_2^s (\text{apparent}) = n^s \frac{(K - 1)N_1N_2}{1 + (K - 1)N_2}$$

will, under certain conditions, predict negative apparent adsorption. When such conditions prevail, explain to which of the isotherms of composition change shown in Figure XI-7 the calculated isotherm will most closely correspond.

13. The example of Section XI-5B may be completed as follows. It is found that $\theta = 0.5$ at a butanol concentration of $0.3 \text{ g}/100 \text{ cm}^3$. The heat of solution of butanol is 25 cal/g . The molecular area of adsorbed butanol is 40 \AA^2 . Show that the heat of adsorption of butanol at this concentration is about 50 ergs/cm^2 .

14. The adsorption of polystyrene polymer, of molecular weight 300,000, on carbon from toluene solution was studied. The carbon used had a specific surface area of $120 \text{ m}^2/\text{g}$, and a saturation adsorption of 33 mg of polymer per gram of carbon was found. The adsorption was 28 mg/g at a concentration of 0.1 mg of polymer per milliliter. (a) Assuming the Langmuir equation to be obeyed, calculate the Langmuir b constant. (b) Do the same, using Eq. XI-19, and assuming that $\nu = 50$. (c) Plot the complete isotherms, as calculated according to (a) and to (b) and comment on the degree of experimental precision needed to distinguish between them. (d) Calculate the number of polymer molecules adsorbed per particle of carbon at saturation.

15. Referring to Section XI-6B, the effect of the exclusion of coions (ions of like charge to that of the interface) results in an increase in solution concentration from n_0 to n'_0 . Since the solution must remain electrically neutral, this means that the counterions (ions of charge opposite to that of the interface) must also increase in concentration from n_0 to n'_0 . Yet Fig. V-1 shows the counterions to be positively adsorbed. Should not their concentration therefore *decrease* on adding the adsorbent to the solution? Explain.

16. The uv-visible absorption spectrum of $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ has a maximum at about 450 nm , from which the energy in volts for process XI-42 may be estimated. The standard reduction potential for the R^+/R couple is about 1.26 V at 25°C . Estimate from this information (and standard reduction potentials) the potential in volts for processes XI-43 and XI-44. Repeat the calculation for alkaline solutions.

General References

- Advances in Chemistry*, Vol. 79, American Chemical Society, Washington, D.C., 1968.
- R. Defay and I. Prigogine, *Surface Tension and Adsorption*, transl. by D. H. Everett, Wiley, New York, 1966.
- W. Eitel, *Silicate Science*, Vol. 1, Academic, New York, 1964.
- F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
- J. X. Khym, *Analytical Ion-Exchange Procedures in Chemistry and Biology*, Prentice-Hall, Englewood Cliffs, NJ, 1974.
- J. J. Kipling, *Adsorption from Solutions of Non-Electrolytes*, Academic, New York, 1965.

- E. Lederer and M. Lederer, *Chromatography*, Elsevier, New York, 1955.
- J. A. Marinsky and Y. Marcus, Eds., *Ion Exchange and Solvent Extraction*, Marcel Dekker, New York, 1973.
- K. L. Mittal, *Adsorption at Interfaces*, ACS Symposium Series No. 8, American Chemical Society, Washington, D.C., 1975.
- G. H. Osborn, *Synthetic Ion Exchangers*, 2nd ed., Chapman and Hall, London, 1961.
- G. Schay, *Surface and Colloid Science*, E. Matijevic, Ed., Wiley-Interscience, New York, 1969.
- H. van Olphen and K. J. Mysels, Eds., *Physical Chemistry: Enriching Topics from Colloid and Surface Science*, Theorex, La Jolla, CA, 1975.

Textual References

1. D. H. Everett, *Pure Appl. Chem.*, **31**, 579 (1972).
2. G. Schay, *Pure Appl. Chem.*, **48**, 393 (1976).
3. D. H. Everett, *Pure & Appl. Chem.*, **58**, 967 (1986).
4. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
5. J. P. Badiali, L. Blum, and M. L. Rosenberg, *Chem. Phys. Lett.*, **129**, 149 (1986).
6. J. C. Berg, *Absorbancy*, P. K. Chatterjee, Ed., Elsevier, Amsterdam, 1985.
7. D. H. Everett, *Trans. Faraday Soc.*, **60**, 1803 (1964); **61**, 2478 (1965). Also S. G. Ash, D. H. Everett, and G. H. Findenegg, *Trans. Faraday Soc.*, **64**, 2645 (1968).
8. P. Somasundaran and D. W. Fuerstenau, *Trans. SME*, **252**, 275 (1972).
9. A. Klinkenberg, *Rec. Trav. Chim.*, **78**, 83 (1959).
10. J. Zeldowitsh, *Acta Physicochim. (USSR)*, **1**, 961 (1934).
11. G. Halsey and H. S. Taylor, *J. Chem. Phys.*, **15**, 624 (1947).
12. H. Freundlich, *Colloid and Capillary Chemistry*, Methuen, London, 1926.
13. K. Urano, Y. Koichi, and Y. Nakazawa, *J. Colloid Interface Sci.*, **81**, 477 (1981).
- 13a. M. Greenbank and M. Manes, *J. Phys. Chem.*, **86**, 4216 (1982).
- 13b. R. S. Hansen and W. V. Facker, Jr., *J. Phys. Chem.*, **57**, 634 (1953).
14. G. Belfort, *AIChE J.*, **27**, 1021 (1981).
- 14a. A. L. Myers and S. Sircar, *Advances in Chemistry*, No. 202, American Chemical Society, Washington, D.C., 1983.
15. B. V. Derjaguin and Yu. V. Shulepov, *Surf. Sci.*, **81**, 149 (1979).
16. K. J. Mysels and H. L. Frisch, *J. Colloid Interface Sci.*, **99**, 136 (1984).
17. H. L. Frisch and K. J. Mysels, *J. Phys. Chem.*, **87**, 3988 (1983).
18. I. Traube, *Annals*, **265**, 27 (1891), and preceding articles.
19. H. N. Holmes and J. B. McKelvey, *J. Phys. Chem.*, **32**, 1522 (1928).
20. G. Altshuler and G. Belfort, *Advances in Chemistry*, No. 202, M. J. McGuire and I. H. Suffet, Eds., American Chemical Society, Washington, D.C., 1983.
21. B. Kronberg and Per Stenius, *J. Colloid Interface Sci.*, **102**, 410 (1984).

22. S. Miller, *Environ. Sci. & Tech.*, **14**, 1037 (1980).
23. G. Belfort, G. L. Altshuler, K. K. Thallam, C. P. Feerick, Jr., and K. L. Woodfield, *AIChE J.*, **30**, 197 (1984).
24. P. Somasundaran, R. Middleton, and K. V. Viswanathan, ACS Symposium Series, No. 253, American Chemical Society, Washington, D.C., 1984.
25. E. Tronel-Peyroz, D. Schuhmann, H. Raous, and C. Bertrand, *J. Colloid Interface Sci.*, **97**, 541 (1984).
26. B. von Szyszkowski, *Z. Phys. Chem.*, **64**, 385 (1908); H. P. Meissner and A. S. Michaels, *Ind. Eng. Chem.*, **41**, 2782 (1949).
27. E. Chibowski, *J. Colloid Interface Sci.*, **92**, 279 (1983).
28. R. S. Hansen and R. P. Craig, *J. Phys. Chem.*, **58**, 211 (1954).
- 28a. F. E. Bartell, T. L. Thomas, and Y. Fu, *J. Phys. Colloid Chem.*, **55**, 1456 (1951).
29. M. E. Zawadzki, A. W. Adamson, M. Fetterolf, and H. E. Offen, *Langmuir*, **2**, 541 (1986).
30. J. J. Kipling, *Adsorption from Solutions of Non-Electrolytes*, Academic, New York, 1965.
31. W. A. Schroeder, *J. Am. Chem. Soc.*, **73**, 1122 (1951).
32. O. H. Wheeler and E. M. Levy, *Can. J. Chem.*, **37**, 1235 (1959).
33. W. R. Smith and W. D. Schaeffer, *Proc. Rubber Technol. Conf.*, 2nd, London, 1948.
34. C. G. Gasser and J. J. Kipling, *Proc. Conf. Carbon*, 4th, Buffalo, 1959, p. 55.
35. S. P. Zhdanov, A. V. Kiselev, and L. F. Pavolova, *Kinet. Catal. (USSR)*, **3**, 391 (1962).
36. R. D. Hansen and R. S. Hansen, *J. Colloid Sci.*, **9**, 1 (1954).
37. J. L. Morrison and D. M. Miller, *Can. J. Chem.*, **33**, 350 (1955).
38. N. Hackerman and A. H. Roebuck, *Ind. Eng. Chem.*, **46**, 1481 (1954). See also F. A. Matsen, A. C. Makrides, and N. Hackerman, *J. Chem. Phys.*, **22**, 1800 (1954).
39. H. A. Smith and K. A. Allen, *J. Phys. Chem.*, **58**, 449 (1954).
40. E. B. Troughton, C. D. Bain, and G. M. Whitesides, *Langmuir*, **4**, 365, 546 (1988); L. Strong and G. M. Whitesides, *ibid.*, **4**, 546 (1988); C. D. Bain and G. M. Whitesides, *Science*, **240**, 62 (1988).
41. M. D. Porter, T. B. Bright, D. L. Allara, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **109**, 3559 (1987).
42. R. S. Hansen, Y. Fu, and F. E. Bartell, *J. Phys. Colloid Chem.*, **53**, 769 (1949).
43. O. M. Dzhigit, A. V. Kiselev, and K. G. Krasilnikov, *Dokl. Akad. Nauk SSSR*, **58**, 413 (1947).
44. F. E. Bartell and D. J. Donahue, *J. Phys. Chem.*, **56**, 665 (1952).
45. E. L. Cook and N. Hackerman, *J. Phys. Colloid Chem.*, **55**, 549 (1951).
46. F. R. Eirich, *J. Colloid Interface Sci.*, **58**, 423 (1977).
47. F. Rowland, R. Bulas, E. Rothstein, and F. R. Eirich, *Ind. Eng. Chem.*, September 1965, p. 46.
48. C. Peterson and T. K. Kwei, *J. Phys. Chem.*, **65**, 1330 (1961).

49. A. Takahashi and M. Kawaguchi, *Adv. Polym. Sci.*, **46**, 1 (1982).
50. W. Heller, *Pure Appl. Chem.*, **12**, 249 (1966).
51. H. L. Frisch, M. Y. Hellman, and J. L. Lundberg, *J. Polym. Sci.*, **38**, 441 (1959).
52. R. Simha, H. Frisch, and F. Eirich, *J. Phys. Chem.*, **57**, 584 (1953); *J. Chem. Phys.*, **25**, 365 (1953); R. Simha, *J. Polym. Sci.*, **29**, 3 (1958).
53. See A. Silverberg, *Faraday Discuss. Chem. Soc.*, **59**, 203 (1975).
54. C. A. J. Hoeve, *J. Polym. Sci. Symp.*, **61**, 389 (1977).
55. R. J. Roe, *J. Chem. Phys.*, **60**, 4192 (1974).
56. J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **83**, 1619 (1979); *ibid.*, **84**, 178 (1980).
57. R. Simha, H. L. Frisch, and F. R. Eirich, *J. Phys. Chem.*, **57**, 584 (1953).
58. E. Di Marcio and R. Rubin, *Am. Chem. Soc. Polym. Prepr.*, **11**, 1239 (1970); E. Di Marcio, *J. Chem. Phys.*, **42**, 2101 (1965).
59. S. G. Ash, D. Everett, and G. H. Findenegg, *Trans. Faraday Soc.*, **66**, 708 (1970).
60. H. L. Frisch, *J. Phys. Chem.*, **59**, 633 (1955).
61. P. G. de Gennes, *Rep. Prog. Phys.*, **32**, 187 (1969); *Compt. Rend.*, **291**, Ser. B, 21 (1980).
- 61a. M. R. Munch and A. P. Gast, *Macromolecules*, **21**, 1366 (1988).
62. B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961); also, F. McCrackin, *J. Chem. Phys.*, **47**, 1980 (1967).
- 62a. M. Kawaguchi and A. Takahashi, *Macromolecules*, **16**, 1465 (1983).
63. F. W. Rowland and F. R. Eirich, *J. Polym. Sci.*, **4**, 2421 (1966).
64. R. R. Stromberg, D. J. Tutas, and E. Passaglia, *J. Phys. Chem.*, **69**, 3955 (1965).
65. M. Kawaguchi, S. Hattori, and A. Takahashi, *Macromolecules*, **20**, 178 (1987).
66. J. D. Andrade, *Surface and Interfacial Aspects of Biomedical Polymers*, Vol. 2, Plenum Press, New York, 1985.
67. J. D. Andrade and V. Hlady, *Adv. Polym. Sci.*, **79**, 1, 1986.
68. R. E. Baier, *Adsorption of Micro-organisms to Surfaces*; G. Bitton and K. C. Marshall, Eds., Wiley-Interscience, New York, 1980.
69. Q. S. Bhatia, D. H. Pan, and J. T. Koberstein, *Macromolecules*, **21**, 2166 (1988).
70. R. R. Stromberg, W. H. Grant, and E. Passaglia, *J. Res. Nat. Bur. Stand.* **68A**, 391 (1984).
71. M. A. C. Stuart, J. M. H. M. Scheutjens, and G. Fleer, *J. Polym. Sci.*, **18**, 559 (1980); G. J. Fleer and B. H. Bijsterbosch, *J. Colloid Interface Sci.*, **90**, 310 (1982).
72. G. Penners, Z. Priel, and A. Silberberg, *J. Colloid Interface Sci.*, **80**, 437 (1981).
- 72a. W. Norde, F. MacRitchie, G. Nowicka, and J. Lyklema, *J. Colloid Interface Sci.*, **112**, 447 (1986).
73. H. G. de Bruin, C. J. Van Oss, and D. R. Assolom, *J. Colloid Interface Sci.*, **76**, 254 (1980).
74. Ph. Gramain and Ph. Myard, *J. Colloid Interface Sci.*, **84**, 114 (1981).

75. V. M. Ziegler and L. L. Handy, *J. Soc. Petrol. Engl.*, **21**, 218 (1981).
76. P. J. Dobson and P. Somasundaran, *J. Colloid Interface Sci.*, **97**, 481 (1984).
77. D. N. Misra, *J. Dental Res.*, **65**, 706 (1986).
78. P. Somasundaran and H. S. Hanna, *J. Soc. Petrol. Eng.*, June, 1985, p. 343.
79. J. Tamura, J. T. Tse, and A. W. Adamson, *J. Japan Petrol. Inst.*, **26**, 309 (1983); **27**, 385 (1984).
80. M. E. Zawadski and A. W. Adamson, *Fundamentals of Adsorption*, A. I. Liapis, Ed., Eng. Foundation, New York, 1987, p. 619.
81. M. E. Zawadski, Y. Harel, and A. W. Adamson, *Langmuir*, **3**, 363 (1987).
82. M. E. Soderquist and A. G. Walton, *J. Colloid Interface Sci.*, **75**, 386 (1980).
83. C. Peterson and T. K. Kwei, *J. Phys. Chem.*, **35**, 1330 (1961).
84. F. Rowland, R. Bulas, E. Rothstein, and F. R. Eirich, *Ind. Eng. Chem.*, **57**, 46 (1965).
85. D. Graham, *J. Phys. Chem.*, **59**, 896 (1955).
86. J. J. Kipling and R. B. Wilson, *J. Appl. Chem.*, **10**, 109 (1960).
87. J. F. Padday, *Pure and Applied Chemistry, Surface Area Determination*, Butterworths, London, 1969.
88. S. S. Barton, *Carbon*, **25**, 343 (1987).
89. M. A. Rahman and A. K. Ghosh, *J. Colloid Interface Sci.*, **77**, 50 (1980).
90. D. H. Everett, *Trans. Faraday Soc.*, **61**, 2478 (1965).
91. G. Schay and L. G. Nagy, *J. Colloid Interface Sci.*, **38**, 302 (1972).
92. H. J. Van den Hul and J. Lyklema, *J. Colloid Interface Sci.*, **23**, 500 (1967).
93. A. Y. Meyer, D. Farin, and D. Avnir, *J. Am. Chem. Soc.*, **108**, 7897 (1986).
94. J. J. Kipling, *Q. Rev. (London)*, **5**, 60 (1951).
95. S. G. Ash, R. Bown, and D. H. Everett, *J. Chem. Thermodyn.*, **5**, 239 (1973).
96. K. M. Phillips and J. P. Wightman, *J. Colloid Interface Sci.*, **108**, 495 (1985).
97. J. J. Kipling and D. A. Tester, *J. Chem. Soc.*, **1952**, 4123.
98. A. L. Myers and S. Sircar, *J. Phys. Chem.*, **76**, 3415 (1972).
99. G. D. Parfitt and P. C. Thompson, *Trans. Faraday Soc.*, **67**, 3372 (1971).
100. G. Schay, *Surf. Colloid Sci.*, **2**, 155 (1969); *J. Colloid Interface Sci.*, **42**, 478 (1973).
- 100a. A. Dabrowski, M. Jaroniec, and J. Oscik, *Ads. Sci. Tech.*, **3**, 221 (1986).
101. S. Sircar, *J. Chem. Soc., Faraday Trans. I*, **82**, 831 (1986).
102. D. Schiby and E. Ruckenstein, *Colloids & Surfaces*, **15**, 17 (1985).
103. S. Sircar, *J. Chem. Soc., Faraday Trans. I*, **82**, 843 (1986); *Langmuir*, **3**, 369 (1987).
104. J. J. Kipling, *Proc. Int. Congr. Surf. Act., 3rd, Mainz, 1960*, Vol. 2, p. 77.
105. G. J. Young, J. J. Chessick, and F. H. Healey, *J. Phys. Chem.*, **60**, 394 (1956).
106. S. Ozawa, M. Goto, K. Kimura, and Y. Ogino, *J. Chem. Soc., Faraday Trans. I*, **80**, 1049 (1984); S. Ozawa, K. Kawahara, M. Yamabe, H. Unno, and Y. Ogino, *ibid.*, **80**, 1059 (1984).
107. A. L. Myers, *Langmuir*, **3**, 121 (1987).
- 107a. R. O. James, *Polymer Colloids*, R. Buscall, T. Corner, and J. F. Stageman, Eds., Elsevier Applied Science, New York, 1985.

108. H. B. Weiser, *Colloid Chemistry*, Wiley, New York, 1950.
109. See K. Fajans, *Radio Elements and Isotopes. Chemical Forces and Optical Properties of Substances*, McGraw-Hill, New York, 1931.
110. I. M. Kolthoff and R. C. Bowers, *J. Am. Chem. Soc.*, **76**, 1503 (1954).
111. A. M. Posner and J. P. Quirk, *J. Colloid Sci.*, **19**, 798 (1964).
112. F. F. Aplan and D. W. Fuerstenau, in *Froth Flotation*, D. W. Fuerstenau, Ed., American Institute of Mining and Metallurgical Engineering, New York, 1962.
113. W. D. Bancroft, *J. Phys. Chem.*, **19**, 363 (1915).
114. S. Kondo, T. Tamaki, and Y. Ozeki, *Langmuir*, **3**, 349 (1987).
115. P. Connor and R. H. Ottewill, *J. Colloid Interface Sci.*, **37**, 642 (1971).
116. S. G. Dick, D. W. Fuerstenau, and T. W. Healy, *J. Colloid Interface Sci.*, **37**, 595 (1971).
117. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.*, **68**, 3562 (1964).
- 117a. J. F. Scamehorn, R. S. Schechter, and W. H. Wade, *J. Colloid Interface Sci.*, **85**, 463 (1982).
118. D. W. Fuerstenau, *Chem. Biosurfaces*, **1**, 143 (1971).
119. W. Paik, M. A. Genshaw, and J. O'M. Bockris, *J. Phys. Chem.*, **74**, 4266 (1970).
120. M. Kawaguchi, K. Hayashi, and A. Takahashi, *Colloids & Surfaces*, **31**, 73 (1988).
121. R. K. Schofield, *Nature*, **160**, 408 (1947).
122. R. K. Schofield and O. Talibuddin, *Discuss. Faraday Soc.*, **3**, 51 (1948).
123. D. G. Edwards and J. P. Quirk, *J. Colloid Sci.*, **17**, 872 (1962).
124. G. H. Bolt and R. D. Miller, *Soil Sci. Am. Proc.*, **19**, 285 (1955); A. V. Blackmore and R. D. Miller, *ibid.*, **25**, 169 (1961). H. van Olphen, *J. Phys. Chem.*, **61**, 1276 (1957).
125. R. M. Barrer and R. M. Gibbons, *Trans. Faraday Soc.*, **59**, 2569 (1963), and preceding references.
126. G. L. Gaines, Jr., and H. C. Thomas, *J. Chem. Phys.*, **23**, 2322 (1955).
127. K. W. T. Goulding and O. Talibudeen, *J. Colloid Interface Sci.*, **78**, 15 (1980).
128. R. M. Barrer and R. P. Townsend, *Zeolites*, **5**, 287 (1985); *J. Chem. Soc. Faraday Trans. 2*, **80**, 629 (1984).
129. P. C. Herder, Per M. Claesson, and C. E. Blom, *J. Colloid Interface Sci.*, **119**, 155 (1987); P. M. Claesson, P. Herder, P. Stenius, J. C. Eriksson, and R. M. Pashley, *ibid.*, **109**, 31 (1986).
130. G. E. Boyd, A. W. Adamson, and L. S. Myers, Jr., *J. Am. Chem. Soc.*, **69**, 2836 (1947).
131. J. J. Grossman and A. W. Adamson, *J. Phys. Chem.*, **56**, 97 (1952).
132. R. Schlögl and F. Helfferich, *J. Chem. Phys.*, **26**, 5 (1957).
133. J. A. Marinsky and Y. Marcus, Eds., *Ion Exchange and Solvent Extraction*, Marcel Dekker, New York, 1973.
134. R. J. Hunter, *Foundations of Colloid Science*, Vol. I, Clarendon Press, Oxford, 1987.
135. K. Viaene, J. Caigui, R. A. Schoonheydt, and F. C. De Schryver, *Langmuir*, **3**, 107 (1987).

136. R. A. Schoonheydt, P. De Pauw, D. Vliers, and F. C. De Schrijver, *J. Phys. Chem.*, **88**, 5113 (1984).
137. J. K. Thomas, *J. Phys. Chem.*, **91**, 267 (1987).
138. P. de Mayo, L. V. Natarajan, and W. R. Ware, *J. Phys. Chem.*, **89**, 3526 (1985).
139. C. Francis, J. Lin, and L. A. Singer, *Chem. Phys. Lett.*, **94**, 162 (1983).
140. R. K. Bauer, P. de Mayo, W. R. Ware, and K. C. Wu, *J. Phys. Chem.*, **86**, 3781 (1982).
141. P. Levitz and H. Van Damme, *J. Phys. Chem.*, **90**, 1302 (1986).
142. P. Chandar, P. Somasundaran, and N. J. Turro, *J. Colloid Interface Sci.*, **117**, 31 (1987).
- 142a. W. Shi, S. Wolfgang, T. C. Streckas, and H. D. Gafney, *J. Phys. Chem.*, **89**, 974 (1985).
143. D. Pines, D. Huppert, and D. Avnir, *J. Chem. Phys.*, **89**, 1177 (1988).
144. D. Avnir, *J. Am. Chem. Soc.*, **109**, 2931 (1987).
145. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972); J. N. Demas and A. W. Adamson, *ibid.*, **95**, 5159 (1973).
146. J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca, and M. Grätzel, *Photogeneration of Hydrogen*, A. Harriman and M. A. West, Eds., Academic Press, New York, 1982.
147. K. Kalyanasundaram and M. Grätzel, *Coord. Chem. Rev.*, **69**, 57 (1986).
148. A. Heller, Y. Degani, D. W. Johnson, Jr., and P. K. Gallagher, *J. Phys. Chem.*, **91**, 5987 (1987).
149. J. K. Thomas and J. Wheeler, *J. Photochem.*, **28**, 285 (1985).
150. E. P. Giannelis, D. G. Nocera, and T. J. Pinnavaia, *Inorg. Chem.*, **26**, 203 (1987).
151. A. J. Frank, I. Willner, Z. Goren, and Y. Degani, *J. Am. Chem. Soc.*, **109**, 3568 (1987).
152. S. Abdo, P. Canesson, M. Cruz, J. J. Fripiat, and H. Van Damme, *J. Phys. Chem.*, **85**, 797 (1981).
153. R. C. Simon, E. A. Mendoza, and H. D. Gafney, *Inorg. Chem.*, **27**, 2733 (1988); W. Shi and H. D. Gafney, *J. Am. Chem. Soc.*, **109**, 1582 (1987).
154. T. Nakamura and J. K. Thomas, *Langmuir*, **1**, 568 (1985).
155. J. Kiwi and M. Grätzel, *J. Phys. Chem.*, **90**, 637 (1986).
156. K. Yamaguti and S. Sato, *J. Chem. Soc., Faraday Trans. I*, **81**, 1237 (1985).
157. J. Kiwi and M. Grätzel, *J. Chem. Soc., Faraday Trans. I*, **83**, 1101 (1987).
158. A. Sobczynski, A. J. Bard, A. Campion, M. A. Fox, T. Mallouk, S. E. Webber, and J. M. White, *J. Phys. Chem.*, **91**, 3316 (1987).
159. L. Spanhel, M. Haase, H. Weller, and A. Henglein, *J. Am. Chem. Soc.*, **109**, 5649 (1987).
160. T. Hasegawa and P. de Mayo, *Langmuir*, **2**, 362 (1986).
161. J. Kuczynski and J. K. Thomas, *Langmuir*, **1**, 158 (1985).
162. N. J. Turro, *Tetrahedron*, **43**, 1589 (1987).
163. N. J. Turro, C. Cheng, L. Abrams, and D. R. Corbin, *J. Am. Chem. Soc.*, **109**, 2449 (1987).

164. R. Farwaha, P. de Mayo, and Y. C. Toong, *J. Chem. Soc., Chem. Comm.*, 739 (1983).
165. D. K. Liu, M. S. Wrighton, D. R. McKay, and G. E. Maciel, *Inorg. Chem.*, **23**, 212 (1984).
166. I. Willner and Y. Degan, *Israel J. Chem.*, **22**, 163 (1982).
167. Y. Degani and I. Willner, *J. Chem. Soc., Perkin Trans. II*, 37 (1986).
168. I. Willner, ACS Symposium Series No. 278, M. A. Fox, Ed., American Chemical Society, Washington, D.C., 1985.
169. R. Maidan and I. Willner, *J. Am. Chem. Soc.*, **108**, 8100 (1986).
170. J. C. Abram and G. D. Parfitt, *Proc. 5th Conf. Carbon*, Pergamon, New York, 1962, p. 97.